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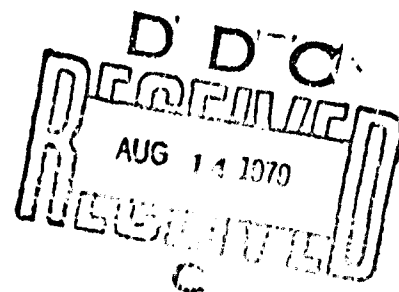
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AFOSR-TR-78-1255

ABSTRACTS

1978 AFOSR CONTRACTORS MEETING  
ON  
AIR-BREATHING COMBUSTION DYNAMICS

October 10-13, 1978



Ramada Inn - Downtown  
Dayton, Ohio

TECHNICAL HOST

*AeroChem* Research Laboratories, Inc.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The report consists of a collection of abstracts of the numerous research progress reports given by AFOSR contractors and of invited papers from other governmental agencies and contractors. These papers presented over a four-day period composed the 1978 annual contractors meeting on Air-Breathing Combustion Dynamics and Kinetics. The principal investigators and their organizational association are also identified.		

# A G E N D A

## 1978 AFOSR CONTRACTORS MEETING on AIR-BREATHING COMBUSTION DYNAMICS AND KINETICS Dayton, Ohio, 10-13 October 1978.

10 Oct 78 Unannounced Justification	
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10 Oct. 78  
Tuesday AM

8:30	Official Registration	Ramada Inn - Dayton, Ohio
9:00	Welcome - AFAPL Host	To be announced
9:10	Welcome - AFOSR	B.T. Wolfson (Program Manager) Air Force Office of Scientific Research (AFOSR) Directorate of Aerospace Sciences
9:15	Morning Chairman	B.T. Wolfson/AFOSR
9:20	1 Air Force Air-Breathing Combustion Research, Development Trends and Research Needs	R.E. Henderson AFAPL/TBC (In-House)
9:50	2 Navy Supported Research and Needs in Air-Breathing Combustion	J.R. Patton/Office Naval Res. S.N.B. Murthy/Purdue University
10:20	BREAK	
10:40	3 DOE Supported Research and Needs in Basic Energy Sciences Associated with Air Breathing Combustion Dynamics and Kinetics	O.W. Adams, J.M. Preses, J.C.T. Pool Department of Energy
11:10	4 NASA Supported Research and Needs in Air-Breathing Combustion	D.A. Petrash NASA-Lewis Research Center
11:40	5 Army Supported Research and Needs in Air-Breathing Combustion	J.J. Murray Army Research Office
12:10	LUNCH	

10 Oct. 78  
Tuesday PM

2:00	Afternoon Chairman	J.R. Patton/ONR
2:05	6 Injection, Atomization, Ignition and Combustion of Liquid Fuels in High Speed Air Streams	J.A. Schetz, A.K. Jakubowski VPI and State University (AFOSR-78-3485)

10 Oct. 78  
Tuesday PM

2:30	7	Mixing, Ignition and Combustion in Flowing Reacting Fuel-Air Mixtures	R.B. Edelman, P.T. Harsha Sciences Applications, Inc. (F49620-77-C-0044)
2:55	8	Flame Efficiency, Stabilization and Performance in Prevaporizing/Pre-mixing Combustors	A.M. Mellor Purdue University (AFOSR-77-3446)
3:20		BREAK	
3:40	9	Research on Ramjet Combustion at AFAPL	R.R. Craig, J.T. Hojnacki, K.G. Schwartzkopf, P.L. Buckley, B.M. Obleski, D.L. Davis AFAPL/RJT (In-House)
4:10	10	Turbulent Vortex Flame Stability and Spreading with Gas Jet Impingement	P.R. Choudhury, M. Gerstein Univ. of Southern California (AFOSR-77-3354)
4:35	11	Flow Flame Interactions and Transient Flame Phenomena	M. Gerstein Univ. of Southern California (AFOSR-77-3354)
5:00		ADJOURN	

11 Oct. 78  
Wednesday AM

8:30		Morning Chairman	J.R. Manheim AFAPL/SFF
8:35	12	Air Force Supported Research Development Trends and Needs in Aircraft Fire and Explosion Technology	J.R. Manheim, B.P. Botteri AFAPL/SFF (In-House)
9:05	13	NASA Supported Research on Fire Resistant Polymers for Aircraft Fire Protection	D.A. Kourtides NASA-Ames Research Center
9:30	14	Aircraft Fuel Fires in Flight	L. Mahood Falcon Research & Dev. Co. G. Gandee AFAPL/SFH (AFAPL Contract)
9:55	15	Ignition of Fuel Sprays by Incendiary Metal Particles	W.A. Sirignano, H.S. Homan Princeton University (AFOSR-76-3052B)
10:20		BREAK	

11 Oct. 78  
Wednesday AM

10:35	16	Ignition of Flowing Liquid Fuels by Hot Surfaces	T.B.C. Shen Southeastern Mass. Univ. (AFOSR-78-3538)
11:00	17	Ignition of a Liquid Fuel Under High Intensity Radiation	T. Kashiwagi National Bureau of Standards (ISSA-78-0002)
11:25	18	Ignition of Fuel Sprays by Hot Surfaces and Stabilization of Aircraft Fires	J.G. Skifstad, A.H. Lefebvre Purdue University (AFOSR-77-3446)
11:50	19	Ignition, Combustion, Detonation and Quenching of Reactive Mixtures	R. Edse Ohio State University (AFOSR-78-3604)
12:15	20	Basic Instability Mechanisms in Chemically Reacting Systems	T.Y. Toong Massachusetts Inst. of Tech. (AFOSR-74-2619)
12:40		LUNCH	

11 Oct. 78  
Wednesday PM

2:00		Afternoon Chairman	F.D. Stull AFAPL/RJT
2:05	21	Investigation of Air-Breathing Engine Catalytic Combustion - Joint NASA/AFAPL Program	L.A. Diehl NASA-Lewis Research Center
2:30	22	Air Force Research Studies and Needs in Catalytic Combustion	L.C. Angello AFAPL/SFF (In-House)
2:55	23	Mechanisms of High Temperature Catalytic Combustion	P.M. Walsh, C. Bruno, D.A. Santavicca, B. Kim, F.V. Bracco Princeton University (AFOSR-76-3052)
3:20		BREAK	
3:40	24	Contributions of Surface Catalysis and Gas Phase Kinetics to Catalyst Combustor Performance	C.M. Ablow, B.J. Wood, H. Wise Stanford Research Institute (F49620-77-C-0123)
4:05	25	Interfacial Chemical Reactions in Flow Systems	D.E. Rosner Yale University (F49620-76-C-0020)

11 Oct. 78  
Wednesday PM

4:30	26	Turbulent Mixing and Combustion in High Speed Flows	G.D. Smith, C.E. Peters AEDC/ARO (PO-78-0012)
5:00		ADJOURN	
6:30		Social Hour (Cash Bar) Banquet	Ramada Inn

12 Oct. 78  
Thursday AM

8:30		Morning Chairman	J.F. Masi Office of Scientific Research Directorate of Aerospace Sciences
8:35	27	Thermodynamics of Ramjet Fuels	W.D. Good Bartlesville Energy Research Center (DOE) (AFOSR-ISSA-78-0009)
9:00	28	Critical Evaluation of High Temperature Kinetic Data	N. Cohen, K. Westberg Aerospace Corporation (AFOSR-ISSA-78-0013)
9:25	29	Kinetics of Oxidation Reactions	R.R. Baldwin, R.W. Walker Hull University, ENGLAND (AFOSR-77-3215)
9:55	30	Combustion Kinetics of Selected Aromatic Hydrocarbons	R.A. Matula, R.C. Farmer Louisiana State University (AFOSR-77-3384)
10:20		BREAK	
10:40	31	Fuels Combustion Research	F.L. Dryer, I. Glassman Princeton University (F49620-78-C-0004)
11:05	32	Absolute Rate Constants of Combustion Reactions Involving Free Radicals	D.F. McMillen, D.M. Golden SRI International (F44620-75-C-0067)
11:30	33	Research on Turbopropulsion Combustion at AFAPL	K. Hopkins AFAPL/TBC (In-House)
11:55	34	Fundamental Modeling of Kinetics Mixing, Evaporation and Combustion in Gas Turbine Combustors	J. Swithenbank Sheffield University, ENGLAND (AFOSR-74-2682)

12 Oct. 78  
Thursday PM

12:20		LUNCH	
2:00		Afternoon Chairman	W.M. Roquemore AFAPL/SFF
2:05	35	Mechanisms of Radiation Augmented Ignition and Combustion	A.E. Cerkanowicz Exxon Research Engineering (F49620-77-C-0085)
2:30	36	Photochemical Experiments of Internal Combustion Engine Operation	R.C. DesMarais, Jr, O.A. Sandven, J.R. Bolten RIGS Corporation
2:40	37	Air Force Supported Research Program and Needs Associated with Gas Turbine Engine Emissions and Other Combustion Related Problems	H.J. Clewell, J.A. Martone Tyndall AFB, Florida AFAPL (In-House)
3:05	38	Fundamental Mechanisms of Carbon Formation in Hydrocarbon and Synthetic Fuel Combustion	W.J. Miller, H.F. Calcote AeroChem Research Labs., Inc. (F49620-77-C-0029)
3:30		BREAK	
3:50	39	Mechanisms of Exhaust Pollutant and Plume Formation in Continuous Combustion	G.S. Samuelson Univ. of California/Irvine (AFOSR-78-3586)
4:15	40	Combustion Dynamic Effects on Ignition, Combustion, Extinction and Smoke Production	F.A. Williams Univ. of California/La Jolla (AFOSR-77-3362)
4:40	41	Combustion Characteristics of New and Alternative Fuels for Air-Breathing Gas Turbine Engines	C.R. Martel AFAPL/SFF (In-House)
5:05	42	Pyrolysis of Hydrocarbon Fuels	W.S. Blazowski, R.B. Edelman Exxon Research Engineering (AFAPL/DOE Contract)
5:30		ADJOURN	

13 Oct. 78  
Friday AM

8:30		Morning Chairman	B.T. Wolfson AFOSR/NA
8:35	43	Multi-Angular Scanning Absorption Emission Techniques for 3-D Combustion Diagnostics	P. Emmerman, R. Goulard George Washington University (AFOSR-77-3439)

13 Oct. 78  
Friday AM

9:00	44	Theoretical Modeling and Experimental Investigations of Reacting Flows in Practical Air-Breathing Engine Combustion Environment Utilizing Advanced Diagnostic Techniques	W.M. Roquemore, P.W. Schreiber AFAPL/SFF (In-House)
9:30	45	Laser Induced Fluorescence Spectroscopy for Species Concentration Measurements in Turbulent Combustion Flows	J.W. Daily Univ. of California/Berkeley (AFOSR-77-3357)
9:55	46	Raman Scattering Measurements for Time and Space Resolved Data in Combustion Systems	M. Lapp, C.M. Penney, S. Warshaw General Electric (F49620-77-C-9904)
10:20		BREAK	
10:40	47	Application of Tunable Lasers and Other Advanced Techniques for Accurate Measurements of Reacting Flow Parameters Under Combustion Conditions	R.K. Hanson, C.T. Bowman Stanford University (F49620-78-C-0026)
11:05	48	Coherent Structures in Turbulent Flames by Laser Anemometry	N.A. Chigier Sheffield University, ENGLAND (AFOSR-77-3414)
11:30	49	Overview of Third International Symposium on LDV and LDV Measurements and Analysis in Turbulent and Mixing Flows	H.D. Thompson, W. H. Stevenson Purdue University (AFAPL F33615-77-C-2010)
12:00		Executive Session AFOSR Contractors and Grantees Only	B.T. Wolfson AFOSR/NA
12:30		ADJOURN	



AIRBREATHING PROPULSION COMBUSTION

Robert E. Henderson  
Manager, Combustion Technology Group  
Turbine Engine Division  
Air Force Aero Propulsion Laboratory

During the 1977 AFOSR Contractor's Conference, an overview presentation was given on current and planned airbreathing combustion research and development activities at the Propulsion Laboratory. Included in this overview was a brief discussion of general programs of interest and areas of emphasis as sponsored by the Ramjet, Fuels and Turbine Engine Divisions. For the most part, only small changes to the Laboratory's Combustion Program have occurred in the past 12 months; consequently, the purpose of this presentation is to reacquaint the combustion research community with a few of the more significant programs currently underway, the principal areas of technical emphasis today, and an update of progress and changes made to the combustion program since the 1977 conference.

1. Ramjet Combustion Technology

Combustion technology programs conducted by the Ramjet Division fall into three principal product lines.

a. The first and most advanced is that of the high performance ramjet, where high speed and long range potential make it an ideal candidate for strategic missions. There are two major strategic ramjet engine programs currently underway, one by the Marquardt Corporation and the other by the Chemical Systems Division, both of which are in support of the Advanced Strategic Air Launched Missile (ASALM) Program. Advanced combustors for these high performance ramjets may be very short L/D designs and be capable of withstanding very high temperatures (without ablative liners) over longer durations. In addition, variable-geometry may soon become an integral design feature for these advanced systems. Variable-geometry inlets and exhaust nozzles are now under study. Although adding mechanical complexity to the propulsion system, variable-geometry will allow the ramjet to maximize its cycle potential without penalty for off-design operation, thereby extending range.

b. The tactical missile propulsion area is still relatively new to the Air Force effort. The tactical ramjet combustor offers a much wider range of combustion problems due to a number of distinct differences between the types of propulsion systems being considered for tactical missile application. Currently under study are the liquid fuel ramjet, the ducted rocket ramjet and the solid fuel ramjet.

(1) Liquid Fuel Ramjet: The combustor for this system can employ a coaxial center dump design or it may use multiple side dumps.

(2) Ducted Rocket Ramjet: This design features a fuel rich gas generator providing a high temperature gas pilot aiding flame stabilization and performance.

(3) Solid Fuel Ramjet: The combustion chamber within this system contains a solid hydrocarbon fuel cast into the combustor. The engine is a relatively simple design but the combustion process is very complex. Fuel injection must be coupled to the combustion process and careful matching of the grain burn rate to the desired flight mission profile is necessary.

c. The high speed propulsion area has been dormant in the Air Force since the late 1960's when several small scale scramjet and dual-mode engines were tested. Recent interest in hypersonics between the Air Force and NASA, however, and the emergence of the National Hypersonics Flight Research Facility, has revived interest in the high speed (hypersonic) propulsion area. Although work in this area has been slow in starting, combustion programs are in planning for a Mach 3-6 subsonic combustion ramjet followed by a number of small research efforts in the dual-mode scramjet area.

## 2. Fuels Combustion Technology

A number of combustion research programs are currently being sponsored by the Fuels and Lubrication Division. Principal areas of interest include external fires and propulsion system related fire hazards, wide-spec fuel effects studies and advanced diagnostic instrumentation development and application in support of in-house combustion research activities. Research in catalytic combustion has been reduced substantially. Main combustor catalytics are now being pursued almost entirely by NASA; however, catalytic flame stabilization studies are currently underway to assess the feasibility of applying catalytic materials to a turbine engine afterburner. Environmental research has been all but eliminated as an area of primary interest now that the Air Force Civil and Environmental Engineering Development Office has taken over the primary sponsoring role. Exhaust emission monitoring during test and the application of some of the remote diagnostic tools for determination of specie concentration levels is virtually the extent of environmental activities at the Laboratory today.

a. Propulsion System Fire Hazards: The fire protection activity stresses research in combustion relative to externally caused fires such as on-board fuel fires initiated by incendiary weapons and engine nacelle fires initiated by fuel, oil and hydraulic fluids ignited by the hot engine surfaces. Consequently, a sound understanding of the combustibility characteristics of all burnable materials, not just the fuel, is essential.

b. Wide-Spec Fuels Combustion Research: Because of the global nature of aircraft operations, jet fuels of the future are likely to be produced from a combination of basic synthetic crudes; ie, coal, oil, shale, tar sand, etc. Production of fuels from blends of synthetic crudes and natural crudes may also be expected. In light

of the wide variations in materials from which world-wide jet fuel production can draw, it is anticipated that economics will dictate the acceptance of future fuels with properties other than those of currently used JP-4, JP-5 and Jet A. Consequently, a number of research and development programs are currently underway or in planning to identify fuel specifications which provide the optimum solution to the following objectives:

- (1) Allow usage of key world-wide resources to assure availability
- (2) Minimize the total cost of aircraft system operation
- (3) Avoid sacrifice of engine performance, flight safety or environmental impact.

c. Combustion Diagnostics Research: An improved technology base is necessary to generate new ideas and improved approaches which will eventually satisfy future turbopropulsion combustion requirements. This technology base, as in the case of any science, must be established through the strong interaction of experiment and theory. Well designed experiments providing insight into the fundamental processes occurring in practical combustion devices are needed. Theories explaining these results and capable of predicting future experimental results are also essential. The intent of combustion diagnostics is to provide the tools needed to collect the necessary data. Programs at AFAPL are currently underway to utilize optical diagnostics to acquire this information.

### 3. Turbopropulsion Combustion Technology

The evolution of aircraft gas turbine combustors over the past forty years has been extremely impressive. The combustion system was considered to be the primary technical limitation in the development of the first aircraft gas turbine engine in 1939. The challenges in advancing combustor design and performance, however, are no less today. New design concepts and technology improvements will be necessary to satisfy legislated environmental regulations. Moreover, future emphasis on engines which can utilize fuels with a broad range of characteristics are expected to require additional combustor technology development.

In order to provide a better appreciation for the role of the gas turbine combustor in the overall development process, a summary of the propulsion system development activity is given. Beyond those externally imposed combustor requirements cited above are the combustion system performance improvements necessary to keep pace with new engine developments. Performance improvements, especially with respect to engine thrust/weight ratio and specific fuel consumption, will require higher combustor temperature rise, greater average turbine inlet temperatures and closer adherence to the design temperature profile at the turbine inlet. High performance designs must

also permit greater Mach number operation within and around the combustor in order to realize the latest advancements in compressor technology; e.g., the high thru flow compressor. Likewise the augmentor is a fairly simple combustion device but with today's complex high performance augmented turbofan engines, the augmentor structural design and fuel distribution system has become increasingly complex -- and is further aggravated by a requirement that the hardware design cannot be finalized until all upstream componentry has been well characterized. Costs (both initial and operating) must be minimized, as experiences with high temperature engines have confirmed the necessity to consider reliability and maintenance aspects of life cycle cost as well as performance and fuel consumption.

#### 4. Requirements/Trends/Research Needs

The airbreathing propulsion combustion technology area is making significant strides today and the demands of tomorrow's system will place even greater challenges on this rapidly advancing field. Environmental quality and energy conservation measures are requiring a thorough understanding of all aspects of combustion -- chemistry, thermodynamics, gas dynamics, etc. Consequently, the research community must continue to take an aggressive role in the investigation and study of such relevant areas as improved fuel-air mixing, staged combustion, diagnostics and fuel chemistry. A brief list of some specific research needs of interest is given below:

##### a. Ramjet Combustion

(1) Development of liquid fuel ramjet scaling criteria, droplet combustion and determination of fuel-air distributions, interactions of flameholder/dump recirculation regions, hysteresis and combustion instability.

(2) Investigation of new concepts such as swirl and jet impingement for improved ramjet combustor performance.

(3) Studies of alternate ramjet cycles such as solid fuel, ducted rocket and dual-mode supersonic combustion ramjet.

(4) Improved ramjet modeling techniques support by detailed flow field characterization.

##### b. Fuels Combustion Research

(1) Improved understanding of practical hydrocarbon fuel pyrolysis to permit inclusion of gross fuel chemistry effects in combustor design models.

(2) Enhanced modeling capability for prediction of wide-spec fuel effects on combustor performance.

(3) Determination of effects of turbulence on CARS, fluorescence, LARS and other remote diagnostic measurements.

(4) Systematic evaluation of the performance of conventional diagnostic probe designs when making measurements of various species in chemically reactive environments.

(5) Carbon and metal slurry fuel pumping, metering, injection and combustion characterization.

c. Turbopropulsion Combustion

(1) Improved understanding of combustor inlet diffuser aerodynamics; e.g., boundary layer bleed systems, vortex-controlled diffusers, diffusion with swirl, etc.

(2) Improved aerodynamic mixing for high temperature rise systems to assure exit temperature uniformity.

(3) Improved ignition for wide-spec fuels under cold start, high altitude operation.

(4) Improved fuel injection techniques for large turn-down ratio systems designed to accommodate wide-spec fuels.

NAVY SUPPORTED RESEARCH AND NEEDS  
IN AIR-BREATHING COMBUSTION

J.R. Patton  
Office of Naval Research

S.N.B. Murthy  
Purdue University

ABSTRACT NOT RECEIVED

DOE SUPPORTED RESEARCH AND NEEDS IN BASIC ENERGY SCIENCES  
ASSOCIATED WITH AIR-BREATHING COMBUSTION DYNAMICS AND KINETICS

O. W. Adams  
J. M. Preses  
J. C. T. Pool

Office of Basic Energy Sciences  
U. S. Department of Energy  
Washington, D.C. 20545

The combustion research program supported by the Office of Basic Energy Sciences (BES), DOE, emphasizes three major components: combustion diagnostics, chemical kinetics and modeling. This program began in FY 1976 and has grown to a level of about \$2.3M in FY 1978. A fourth component, representing the application of quantum theory to the study of combustion reactions, is developing largely via projects carried out at the national laboratories.

The diagnostics component of the program consists primarily of research now being done at the Sandia Livermore Laboratory. This research, and related development work, will be consolidated late in FY 1980 or early FY 1981 into a Combustion Diagnostics Facility, now under construction. Research at this facility will emphasize the application of laser diagnostics to the study of simple and complex combustion systems. It is designed to be a user-oriented facility.

The kinetics component of the combustion program is composed of a number of small scale research projects being carried out largely at universities. Included here is a project, "Data Base for Combustion Modeling," being carried out at NBS.

The modeling component addresses the formulation of numerical methods basic to modeling: a) simple flame structures and b) complex systems. The former emphasizes numerical methods for systems of ordinary differential equations while the latter emphasizes, for example, adaptive methods for partial differential equations.

It is anticipated that the BES combustion research program will show only limited growth in FY 1979, the exceptions being the Sandia facility which will continue to grow as the facility nears completion and some growth resulting from projects at several national laboratories in which principal investigators are changing the direction of their existing projects toward combustion research.

NASA SUPPORTED RESEARCH AND NEEDS IN  
AIR-BREATHING COMBUSTION

Donald A. Petrash

Chief, Combustion and Pollution Research Branch  
Airbreathing Engines Division  
NASA Lewis Research Center

The Combustion and Pollution Research Branch of the Airbreathing Engines Division is engaged in a research and technology program aimed at providing the combustion designer the information and data required to design and develop advanced combustors that have high performance, low pollutant emissions, and the capability to operate on broad specification fuels for both military and civil gas turbine engine applications. A recent re-organization of the Branch has resulted in the formation of the Combustion Fundamentals Section, the Combustor Technology and a Small Combustor Section.

Combustion Fundamentals

In-house experimental programs are active in the areas of autoignition and flashback, fuel air vaporization and mixing, and the effect of compressor exit flow nonuniformities as related to premixed prevaporized combustion. Supporting research grants and contracts are focused not only on problems associated with the premixed prevaporized combustion phenomena but are also directed to areas such as dilution jet mixing, external fuel vaporization and internal combustor aerodynamics.

The stratospheric cruise emission reduction program which was discussed in detail at last year's meeting will move into Phase II in FY '79 aimed at identifying promising combustor designs based on the data obtained in Phase I for lean premixed prevaporized combustion.

Combustor Technology

In FY '79 a new facility will come on line at the Center which will provide the capability to conduct research and technology studies in full scale combustors at pressure levels up to 40 atmospheres. Initial studies conducted in this facility will be to determine the effect of pressure on flame radiation, on combustor liner heat flux and to determine the pressure effects on the formation of  $\text{NO}_x$  and smoke.

NASA/In House



Most advanced combustor concepts, which are designed to minimize pollutant emissions, have multiple burning zones; a pilot zone wherein idle emission (CO and HC) are controlled and a main or high power zone where NO<sub>x</sub> emission are controlled. This zoning has been accomplished by using multiple fuel injection zones. Control can also be achieved with a single fuel injection zone and variable geometry to stage and schedule the airflow through the combustor. Several variable geometry combustors will be evaluated in sector tests with the most promising ultimately being tested in the 40 atmosphere facility.

#### Small Combustor

Current in-house programs are concentrating on problems associated with reverse flow combustors suitable for use in engines of the 1500 shaft horsepower size. Initial studies are directed at fuel injection where both injector design will be varied and injector number and spacing will be investigated. Subsequent studies will determine optimum liner cooling flows to achieve long life. It is in this area of small combustor technology that a growth is anticipated in both manpower and funding. Increased emphasis is being placed in rotorcraft propulsion systems and on propulsion systems for application to cruise missiles. Efforts in FY '79 will concentrate on defining in more detail the technology needs in these areas.

ARMY SUPPORTED RESEARCH AND NEEDS IN AIR-BREATHING COMBUSTION

James J. Murray

U. S. Army Research Office  
P. O. Box 12211  
Research Triangle Park, N. C. 27709

Research in this area is undertaken in support of the following Army needs for improved and new technology: better air and ground vehicle power plants and the conservation of fuels; more efficient fixed base power plants and auxiliary power units; superior propellants needed to fire and propel projectiles and rockets; and more powerful power sources to provide the energy required for high energy weapons such as lasers. Included in this program are both theoretical and experimental studies on problems directly related to the power plants or sources required.

A superior basic understanding of the technical behavior of power plants, propellants and fuels under various conditions in which the modern Army must operate is of considerable importance to achieve needed performance in terms of agility, firepower, conservation of materials and fuels and reduction of logistic supplies needed for effective operations. Consequently, research in energy conversion, thermodynamics, heat transfer, structures, materials, fluid mechanics, fuels and energetic materials is most appropriate and necessary. Research is concentrated in these areas to provide the fundamental knowledge and technology for new concepts necessary to meet the Army's requirement.

The DARCOM laboratories and the Army Research Office are interested in the topics below:

Engine and Fuel Conservation: Vehicle engines and fuels must be understood if better performance, greater reliability, safety, lower maintenance, and more efficient fuel usage can be obtained for both ground vehicles and Army aircraft propulsion systems as well as other mobile and stationary power generating plants. This program requires fundamental studies in engine combustion, heat transfer, thermodynamics, materials, fluid dynamics and chemical reactions to achieve a basic understanding of the interactions of phenomena occurring in internal combustion engines versus the fuel utilized.

Chemical Lasers: The development of an Army high energy chemical laser requires that maximum physical interaction be afforded to the mixing gases (oxidant and fuel). This subfield now calls for mostly experimental studies involving fluid mechanics, boundary layer theory, turbulent flow, heat and mass transfer, and chemical kinetics as well as efficient diffuser concepts.

Army/In House

Propellants: The Army requires knowledge in the broad field of propellants, both for the launching and propulsion of missiles, rockets, and projectiles. Insofar as propellants are concerned, it is necessary to predict the ignition, burning, temperature and other rate effects such as pressure and volume changes, in order to obtain maximum and optimal conditions in the gun-missile systems. These needs call for basic understanding of all the interrelated phenomena from the standpoint of heat and mass transfer, thermodynamics, materials, chemical kinetics, fluid mechanics and shock and vibrations.

In view of the increasing scarcity of domestic fuel reserves, increasing vulnerability of foreign fuel resources and rising fuel costs, the efficiency of fuel combustion processes must be decidedly improved. In addition, engine types that can satisfactorily operate on different types of fuel must be developed and explored. Particular emphasis is placed on the diesel, turbine and standard carburetor-type engines; however, new and innovative engine concepts should also be examined. These objectives require research emphasis on engine combustion, fuel flow optimization in the cylinder chamber, and an improved basic understanding of the minimally required crude oil refinement processes.

# INJECTION, ATOMIZATION, IGNITION AND COMBUSTION OF LIQUID FUELS IN HIGH-SPEED AIR STREAMS

J. A. Schetz and A. K. Jakubowski

Aerospace and Ocean Engineering Department  
Virginia Polytechnic Institute and State University  
Blacksburg, Virginia 24061

Studies which are now underway at VPI include three tasks - two aimed at the physical processes of the system and one aimed at some aspects of the chemical processes in the total problem.

A comprehensive study of the effects of transverse injection angle on liquid jet penetration and break-up in a Mach 3.0 airstream has been completed. The tests were conducted in the VPI 23 cm. x 23 cm. supersonic wind tunnel at  $T_0 = 540^\circ\text{R}$  and  $P_0 = 75$  psi. Injection was studied from a flat-plate model and the top of a diamond-shaped wedge. Separate injectors were made for different diameters and different upstream and downstream injection angles. Penetration was determined from "streak" photographs of  $1 \times 10^{-3}$  sec. duration. The results of the penetration tests were correlated for all angles, and these results were used in combination with those from earlier work to produce a comprehensive correlation equation, which now contains the effects of: 1) liquid flow rate, 2) air Mach number, 3) injection port size, 4) injection port shape, 5) injection angle and 6)  $x/d$ .

The work on ignition of liquid fuels jets in a hot, supersonic air stream is concerned with understanding the processes of auto-ignition of storable, non-toxic, liquid fuels, such as kerosene, injected across a hot, supersonic air stream. The work is largely experimental, with supporting mathematical models being developed to clarify aspects of the results. The experiments are conducted in a special hot-air facility developed for this work. The facility consists of a 76 ft. long, 1.5 in O.D. Inconel 601 tube that is heated electrically (40 volts, 1800 amps) and an ethylene-fired afterburner. Air at 1#/sec leaves the Inconel tube at  $1600^\circ\text{F}$  and can then be raised to approximately  $2300^\circ\text{F}$  by the afterburner. Oxygen make-up is employed to yield the correct oxygen mass fraction in the slightly "vitiated" air. The exhaust from the afterburner is run through a Mach 1.65 nozzle. A fuel injection port is located near the nozzle exit.

The injection and ignition processes are also observed directly by B & W self-luminosity photographs, B & W television and by Thermographic Infrared Imagery using a Thermovision 680 camera. This camera senses the infrared radiation emitted by a heated surface, processes these infrared images internally and produces ten color, isotherm band images of the field of view on a color television screen.

Two thorough test series using kerosene,  $\text{CS}_2$  and water (as a control) for injectants had been completed prior to this year's program. No unequivocal proof of ignition was observed. In our latest work,

tests were performed with three injectants; water, kerosene and carbon disulfide, at temperatures ranging from 1750°F to 2300°F. Also, at the highest temperature, each liquid was injected at 135 psi, 300 psi and 450 psi, and the fuels were also injected at lower pressures. Data was collected with injection both normal and oblique-upstream (135°) with respect to the main flow.

For both the oblique and normal injections, the fuel runs indicate a hotter region downstream of the injection port. This is evidenced by the perturbation of more isotherms than just the white outside isotherm which characterized the water injections. More positive indications of combustion as concerns the injection of CS<sub>2</sub>, are the wall and flow temperatures just downstream of the injection port at an injection pressure of 135 psi. For  $T_0 \text{ ave} = 2030^\circ\text{F}$  there are perturbations of the wall temperature all through the injection stage of the run. At the next higher temperature this phenomena is repeated. The flow temperatures just downstream of the injection port indicate the same thing with the perturbations beginning at  $T_0 = 2030^\circ\text{F}$  and consistently occurring at higher temperatures. This phenomena did not occur for CS<sub>2</sub> at higher injections pressures with higher temperatures.

The work on droplet size measurements in supersonic flows has now progressed to the point where serious data taking is routine. Measurements were made at the conditions used by Joshi and Schetz for penetration and initial break-up studies ( $M = 3.0$ ,  $P_0 \approx 80$  psia and  $1.0 \leq \bar{q} \leq 10.0$ ). Those previous studies here at VPI thus serve as background material for our current work. Careful assessment and trial use of the scattering technique during 1977 showed that the system had to be completely re-designed. This was accomplished, and the new system was constructed in early 1978. The changes involved a new laser, a new photo-multiplier, new spatial filtering and, very importantly, new windows for the supersonic wind tunnel.

A versatile test set-up for studies of injection and mixing in "dump" combustors has been designed and constructed. The apparatus is designed to work with combustor approach flows in the range  $0.3 < M < 0.8$ . A wide range of "step" heights can be easily achieved. Various fuel injection locations upstream of the step have been provided for. The measurement techniques to be employed include: wall pressures, pitot pressure profiles, schlieren photographs, spark photomicrographs, high-speed movies and droplet sizes by light scattering. Calibration runs showed excellent flow uniformity at all Mach numbers. Systematic data taking is now in progress.

MIXING, IGNITION AND COMBUSTION IN  
FLOWING REACTING FUEL-AIR MIXTURES  
CONTRACT: F49620-77-C-0044

R. B. Edelman and P. T. Harsha

Science Applications, Inc.  
20335 Ventura Blvd., Suite 423  
Woodland Hills, California 91364

For airborne weapon delivery at high speeds, advanced air-breathing propulsion engines incorporating subsonic and supersonic combustion and capable of operating over wide ranges of flight conditions are needed.

Realization of the performance potential offered by existing and future engine concepts is hampered by insufficient understanding of the basic mechanisms and their mutual interactions. Turbulent mixing and finite rate chemical reactions involving condensed phase fuels are the main processes of interest. Interpretation of data and the development of realistic predictions of performance based on the coupling of the fluid dynamics and chemical kinetics mechanisms are required in order to develop effective systems in an economic and timely manner.

Current emphasis has been on subsonic combustion involving systems of the integral rocket/ramjet type utilizing the sudden expansion (dump) combustor concept. Simplicity is inherent in this concept and high combustion efficiency with wide flame stabilization limits are potentially available as a consequence of the imbedded recirculation zone(s). Consistent and good performance has, however, not been achieved.

Our effort has been directed toward developing an understanding of the parameters controlling the heat release process as it relates to combustion efficiency and flame stabilization. The methodology under current investigation involves a modular approach wherein the reacting flow field is described in terms of domains each of which is characterized by a well defined flow feature. In the sudden expansion burner there are two flow domains; a recirculation zone(s) and a primary, or "directed" flow. The recirculation zone(s) is treated with stirred reactor theory and the primary flow is treated with ducted jet mixing theory. Finite rate chemistry for hydrocarbon oxidation and turbulent kinetics energy (TKE) methods are included in the model. The two flow regions are fully coupled through the boundary conditions along the dividing streamline separating the non-uniform primary flow from the recirculating flow.

During this past year the model has been developed through comparison with data. In addition, a multiphase turbulent reacting flow module has been formulated to accommodate spray combustion, and work has been initiated on the development of a unified treatment of combustor flow fields.

FLAME EFFICIENCY, STABILIZATION AND PERFORMANCE  
IN PREVAPORIZING/PREMIKING COMBUSTORS

A. M. Mellor

The Combustion Laboratory  
School of Mechanical Engineering  
Purdue University  
West Lafayette, Indiana 47907

Advanced combustor design concepts involving fuel prevaporization and premixing upstream of the flame stabilization zone are considered. Applications include automotive, catalytic, ramjet and aircraft propulsion systems. However, problems of poor combustion efficiency and lean blowoff must be overcome. The Purdue research program considers these problems using a simplified sudden expansion combustor, a compromise between the disc flameholder, which has been studied extensively by Tuttle et al. (1977) for EPA, and the dump ramjet burner of Stull et al. (1974). Flame stabilization results from a bluff body recirculation zone characteristic of ramjet and turbojet afterburners.

During the current grant period, the characteristic time model (Mellor, 1976) was applied to combustion efficiency and lean blowoff data measured using five different geometries, two fuels (Jet A and liquid propane) and several injectors over a wide range of burner inlet conditions typical of modern continuous combustion systems. The characteristic time model separates the combustion process into three subprocesses involving heterogeneous, chemical and fluid mechanic effects, each characterized by an appropriate time scale.

For lean blowoff the important times are: 1) the fuel droplet evaporation time ( $\tau_{eb}$ ), 2) the fuel ignition delay time ( $\tau_{hc}$ ) and 3) the shear layer mixing time ( $\tau_{sl}$ ).  $\tau_{eb}$  will be important only when complete prevaporization has not been achieved in the fuel preparation tube. The characteristic time correlation for lean blowoff is based on the theory of Zukoski and Marble (1956) but modified to include heterogeneous effects:

where  $\tau_{sl} = \tau_{hc} + a \tau_{eb}$

$$\tau_{sl} = L/V$$

$$\tau_{hc} = \frac{e}{\phi} \frac{E}{RT}$$

and

$L$  = length scale

$V$  = air velocity

$T$  = stoichiometric adiabatic flame temperature

$\phi$  = overall equivalence ratio

$R$  = universal gas constant

$\tau_{eb}$  = droplet evaporation time calculated from  
"d<sup>2</sup>" law

$a, E$  = empirically determined constants = .011,  
21000 cal/mole, respectively.

The model includes pressure, temperature, velocity, geometry,  
fuel and injector variations (see Fig. 1).

The combustion efficiency data havenot yet been satisfactori-  
ly correlated using the characteristic time model. In order to  
identify the proper scaling parameters to include in the model,  
detailed species concentration, temperature and velocity measure-  
ments of two flames are in progress. Temperature and species con-  
centration mappings for the inefficient flame have been completed  
and results will be presented.

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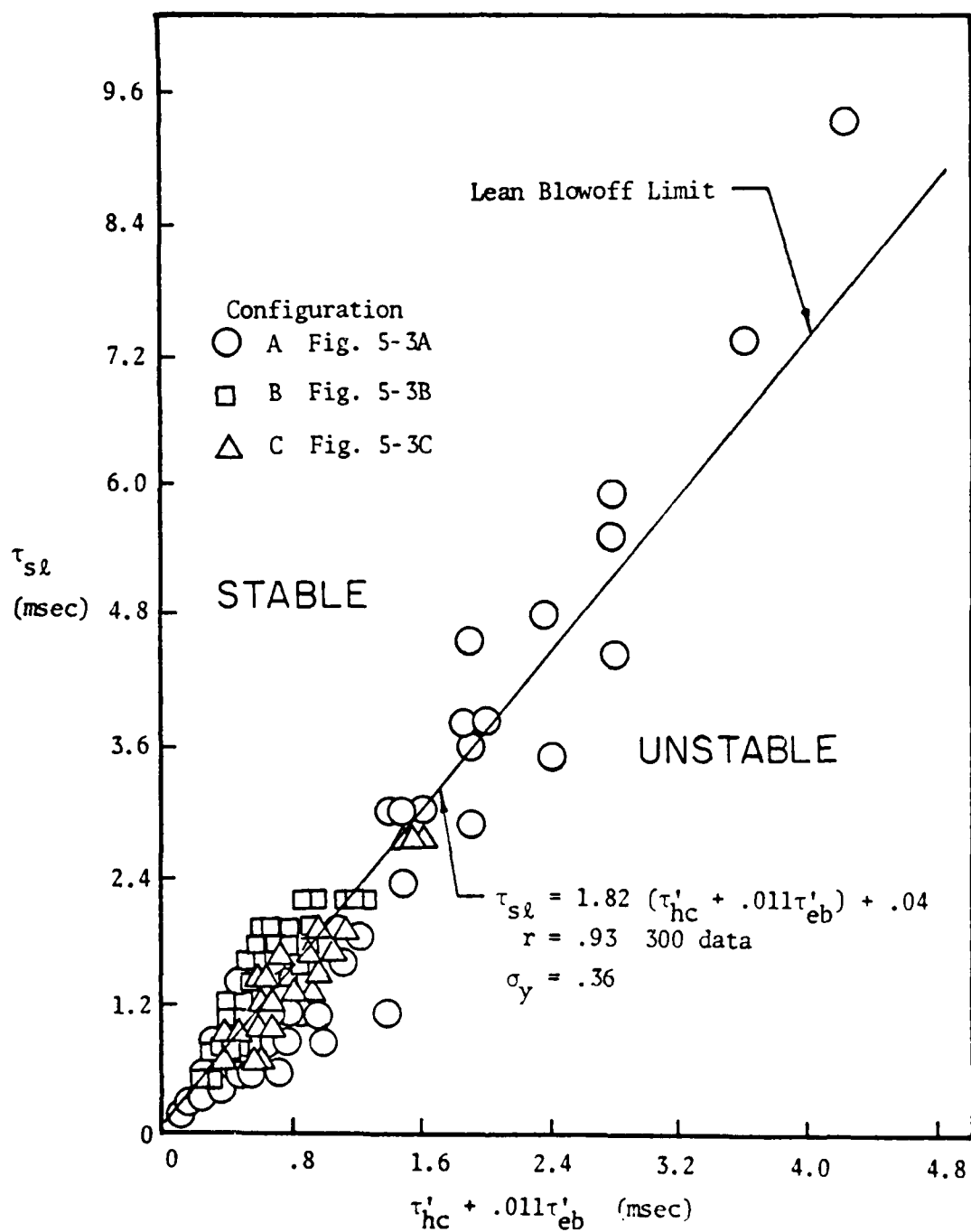


Figure 1. Complete characteristic time correlation for inlet, geometry and fuel variations on three simplified bluff body stabilized flames (negligible fuel penetration effects).

# RAMJET COMBUSTORS

R. R. Craig, J. T. Hojnacki  
K. G. Schwartzkopf, P. L. Buckley  
B. M. Obleski, D. L. Davis

Air Force Aero Propulsion Laboratory  
Ramjet Engine Division  
Ramjet Technology Branch  
Wright-Patterson AFB, Ohio 45433

Dump combustors have become the basis for modern volume limited ramjet missile designs. Since the combustor must contain the rocket boost propellant, use of conventional can combustors is not permitted. Combustion piloting must depend to a large extent on the recirculation zone formed by the sudden area change at the inlet duct, combustor junction. Although several such combustors have been successfully built and tested in recent years, the specific nature of these prior designs have precluded obtaining a sound technical data base or detailed flowfield data necessary for combustor modeling efforts. The objective of the in-house programs being conducted by the Ramjet Engine Division of the Air Force Aero Propulsion Laboratory is to provide such a data base to assist the combustor modelers and to also provide a data base for making a better first cut at a new engine design.

In one of the test programs conducted on our thrust stand in the last year, a series of parametric tests were conducted on annular and Y flameholders. These tests were an attempt to correlate combustion performance data with cold flow mixing results obtained with a quadrupole mass spectrometer under the Ramjet Fluid Dynamics effort. Although good mixing in cold flow is not a sufficient condition for good combustor performance, it certainly is a necessary condition and it is here that the value of cold flow mixing results are realized.

Parametric tests have also been completed on dump combustor with a variable angle swirler. The data are compared with chemical efficiency measurements made by Detroit-Diesel Allison under an LDF contract. Although annular and Y flameholders would sustain combustion in a 6" combustor with a 4" inlet, the swirl burner would not. This is probably due to the swirl reducing the size of the recirculation zone below some critical value. With a 3" inlet, the combustor operated very smoothly.

Test data anomalies alluded to in last year's report were investigated further. It was found that the influence of an upstream flow straightener on dump combustor performance was negligible. It was also found that the use of vitiated air in combustor testing increases the performance about 4% above that obtained with clean air.

AFAPL/In House

Initial results have been obtained with our single component laser anemometer system in a plastic model of an axisymmetric dump combustor. Although the LDA counter processor is not yet interfaced with our mini computer, a technique was found which seems to yield good results using conventional time average and RMS measurement techniques. Good agreement was found between these measurements and previous hot-film anemometer data. Frequency shifting was used on one beam to enable velocity measurements to be made in the recirculation zone.

TURBULENT VORTEX FLAME STABILITY AND SPREADING WITH  
GAS JETS AND SPRAY CONTROL AND HOMOGENEOUS IGNITION  
OF FUEL-AIR EXPLOSIONS

P. Roy Choudhury and Melvin Gerstein

University of Southern California  
Department of Mechanical Engineering  
Los Angeles, California 90007

The effectiveness of a cross-jet system as a means of introducing swirl in a combustor has been investigated parametrically. The swirl angle (angle of jet from the radial direction) has been varied from 0 to 60° for a range of jet stagnation pressures from 5 to 45 psig. The location has been varied from 1/8 inch to 7/8 inch from the sudden expansion step. In addition to these, the number of jet holes and the jet mass flow rate have been varied.

These studies have been conducted both for hot flow using premixed propane air mixture and cold flow at room temperature. Most of the experiments were conducted in a 3 inch diameter axisymmetric burner with a 2 inch inlet. A 4 inch burner with a 3 inch inlet was also used in some of the experiments. Typically, the jet system consisted of 36 equally spaced .04 inch diameter holes located on the wall ahead of the dump plane. The jet flow rate is usually maintained between 3 to 5% of the primary air flow rate.

In addition to the experiments at USC, tests were also run at the AFAPL, Dayton, Ohio, in a 6 inch burner with a 4 inch inlet. Several hole sizes for the cross-jets and several swirl angles were investigated. The ranges of pressure and temperature in these tests were consistent with a typical ramjet application and the burner nozzle was always choked. The first objective of the cooperative program was to determine whether the cross-jet system can perform effectively in a high temperature, high pressure environment with choked burner nozzle. The second objective was to ascertain if it would be possible to predict the performance of a larger burner operating at higher pressure and temperature, from the known behavior of small laboratory scale burners at lower pressures and temperatures.

The cross-jet system (36 equally spaced .04 inch to .08 inch holes 1/2 inch ahead of the dump plane) with a mass flow rate of 4% to 5% of the primary flow rate caused approximately a maximum of 20 percentage point increase in combustion efficiency. This increase in combustion efficiency can be attributed to an increase in flame spreading similar to that observed in the low pressure and low temperature systems. For very lean mixtures, the increase in combustion efficiency with the cross-jet system was marginal and in several cases the efficiency actually decreased because of the local dilution of combustible mixture. This phenomenon was usually observed at very lean mixtures both with normal and swirl jets.

The flame blowoff data from the low pressure and low temperature systems (USC tests) can be used to predict the blowoff in AFAPL experiments. This is consistent with the observation in USC tests that the flame blowoff in dump burners is a local phenomenon and is independent of the burner size as long as the step height is sufficiently large to provide an adequate recirculation zone volume. The length of the recirculation zone is 8 to 9 times the step height in an axisymmetric chamber.

As long as the jet mass flow rate relative to the primary flow rate is kept constant, the blowoff performance in the USC tests was independent of the jet pressures between 5 to 45 psig. Unfortunately, the shop air at 100 psig had to be used in the AFAPL tests. Thus, the insensitivity of flame blowoff to the jet pressure in larger systems could not be verified.

Results of the two experimental programs show that the small-scale tests at low pressure and temperature can be used to predict the increase in combustion efficiency, flame blowoff, and the pressure distribution in larger systems with realistic stagnation pressure and temperatures.

Experiments have been formed to pressures of 60 psi to investigate the hot surface evaporation and decomposition of practical liquid fuels. The increased pressure leads to a higher liquid boiling point and, hence, higher liquid temperatures, promoting liquid phase decomposition. The effect is confirmed experimentally.

The computer program to describe the simultaneous evaporation and decomposition process has been written and is currently being debugged. The non-decomposition portion has been verified. The decomposition program is almost ready to run.

The apparatus to test programmed ignition of fuel-air clouds has been built and is being calibrated using a hydrocarbon spray and spark ignition. A source of trimethyl aluminum and triethyl aluminum has been found and preparations are being made for the experimental study. The theoretical program is finished and computer runs have been made with TMA and TEA added to decane and hexadecane.

Aircraft Fire Protection  
(Overview of Air Force Aero Propulsion Laboratory  
Research and Development Activities)  
AFAPL/In House

J. R. Manheim and B. P. Botteri

Fire Protection Branch  
Air Force Aero Propulsion Laboratory  
Wright Patterson AFB, Ohio

Fire and explosion hazards provide inherent threats to aircraft fire safety, and in the case of military aircraft, the problem is further aggravated by the additional fire and explosion possibilities associated with operations in a hostile (combat) environment. Consequently, the realization of an adequate flight fire safety posture and the enhancement of combat survivability requires the judicious application of fire and explosion prevention measures in the early design of the aircraft complemented as necessary with fire containment, detection and extinguishment capabilities in remaining high fire risk areas. Enhancement of combat survivability necessitates the extension of active and passive fire and explosion protection considerations to a much larger portion of the aircraft because of their potential exposure to combat ignition threats. Obviously, specific protection measures adopted for particular types of aircraft will vary because of the necessity of arriving at a near optimum balance between specific system mission performance, life cycle costs and safety/survivability enhancement.

The Air Force Aero Propulsion Laboratory's current and planned research and development activities in the aircraft fire protection area will be briefly reviewed. These encompass such hazard aspects as static electricity, hydraulic fluid flammability, fire and explosion vulnerability assessment methodology, and advanced fire detection and fire and explosion protection systems.

Many of the current activities address "now" type fire concerns. Engineering emphasis in most instances is driven by aircraft mishaps and/or past combat experiences wherein fire and/or explosion was the catastrophic event.

With respect to fire research requirements, it is very apparent that future technological progress with respect to risk assessment, risk minimization, and protective measure optimization will rely on close integration of the understanding of fire dynamics via theoretical and experimental modeling and engineering of materials and systems to counteract the threat. Accordingly, in the case of military aircraft, the pertinent fire scenarios under combat and non-combat conditions need to be studied, characterized, modeled, and validated via full-scale testing when necessary. Laboratory testing methods must be developed which from the physico-chemical process standpoint are well understood and relate in a meaningful manner to the fire scenario of concern. Obviously, the challenge is not a simple one, but in the long-term, an essential one. Several of the later papers in this session represent a very small start toward such a challenge.

NASA SUPPORTED RESEARCH ON FIRE RESISTANT  
POLYMERS FOR AIRCRAFT FIRE PROTECTION

Demetrius A. Kourtides

National Aeronautics and Space Administration

Moffett Field, California 94035

Polymeric materials are used in both commercial and military aircraft interiors as films, compression- and injection-molded parts, and thermoformed parts. Typical components include: canopies, windows, service units, luminaries, seat side panels, flight station parts, and composite panels. Even though currently used materials meet regulatory requirements there is considerable effort both by industry, aircraft manufacturers, and government to study and define materials that would offer improved fire resistance and, upon combustion, produce less smoke, irritating fumes, and toxic gases.

There is an increasing demand both in the commercial and military sectors for thermoplastic and thermoset resins which, depending on the application, must exhibit one or more high performance characteristics. The resin chosen for a particular application must not only meet the end requirements but also must have good processing characteristics. High performance thermoplastic polymers and thermoset resins must possess one or more of the following characteristics: good thermal oxidative stability; good elevated temperature mechanical properties; high humidity resistance; good fatigue and toughness properties; and chemical and radiation resistance. In addition to the above properties, the polymers selected must exhibit good fire-resistant properties, especially if the material is intended for use in habitable areas. The materials must exhibit the following properties when subjected to various flammability tests: low rate of heat release and fuel contribution; low smoke emission; and low concentration of toxic gases when subjected to a fire environment.

In this presentation, some of these high performance thermoplastics and thermoset resins will be described with particular emphasis on the flammability properties. The materials reviewed include both commercially available resins and other polymers under development by industry and government laboratories. This paper will review some of the thermochemical and flammability properties of these high performance polymers.

Specifically, the thermal and flammability properties of some thermoset and thermoplastic polymers currently used and others considered for potential use in aircraft interiors are described. The studies involved (a) the development and evaluation of aircraft interiors

composite panels and (b) the thermochemical and flammability characterization of thermoplastic resins.

In the area of thermoset resins and composites, the processing and evaluation of composites fabricated from currently used resins and advanced fire resistant resins is described. Laboratory test methodology used to qualify candidate composite materials includes thermochemical characterization of the polymeric compounds and evaluation of the completed composite assemblies for flammability, fire endurance and smoke evolution. The use of these test methods will be discussed in comparing advanced laminating resins and composites consisting of modified phenolics, bismaleimide and polyimide, with conventional baseline materials consisting of epoxy. Particular attention is given to the development of assessment criteria such as fire endurance, or fire containment capability, and smoke produced when these composites are subjected to a fire environment. Of all the laminating resins evaluated, the phenolic resin exhibited the best combination of fire-resistant and processing properties. A significant decrease in propensity to burn, smoke evolution and heat release was achieved by the use of the modified phenolic resin in the face-sheet instead of the baseline epoxy.

In the area of thermoplastic resins, the thermochemical and flammability characteristics of some typical thermoplastic materials currently in use and others being considered for use in aircraft interiors are described. The properties studies included (1) thermogravimetric analysis in anaerobic and oxidative environments, (2) oxygen index, (3) smoke evolution, (4) relative toxicity of the volatile products of pyrolysis, and (5) selected physical properties. The generic polymers that were evaluated included: acrylonitrile butadiene styrene, bisphenol A polycarbonate, 9,9 bis(4-hydroxyphenyl) fluorene polycarbonate-poly (dimethylsiloxane) block polymer, phenolphthalein-bisphenol A polycarbonate, phenolphthalein polycarbonate, polyether sulfone, polyphenylene oxide, polyphenylene sulfide, polyaryl sulfone, chlorinated polyvinyl chloride homopolymer, polyvinyl fluoride, and polyvinylidene fluoride. Processing parameters, including molding characteristics of some of the advanced polymers, are described. A relative ranking was obtained as to the relative flammability properties of these thermoplastic resins. This ranking was based on data from the thermal and flammability tests indicated. Assuming equal weight assignment to each flammability parameter, the polymers and their relative percent values could be rated as follows, in order of increased fire safety: polyphenylene oxide; acrylonitrile butadiene styrene; bisphenol A polycarbonate; chlorinated polyvinyl chloride homopolymer; bisphenol A polycarbonate; polyaryl sulfone; polyvinylidene fluoride; polyvinyl fluoride; polyether sulfone; 9,9 bis(4-hydroxyphenyl)-fluorene polycarbonate-poly (dimethylsiloxane) block polymer; and polyphenylene sulfide.



For both thermoset and thermoplastic polymers, a correlation was established between the oxygen indices of the polymers and their anaerobic char yield. Generally, polymers with high anaerobic char yield exhibited high oxygen index.

# AIRCRAFT FUEL FIRES IN FLIGHT

Levelle Mahood

Falcon Research & Development  
Denver, Colorado

Aircraft fuel fires in flight are always serious and, if uncontrolled, usually lead to severe damage or loss of the aircraft. Fires involving damaged fuel tanks are common causes of combat losses. Significant advances have been recently made to better understand in-flight fuel tank fires caused by nonnuclear combat threats.

Under sponsorship of the Air Force Aero Propulsion Laboratory (AFAPL/SFH) and the Joint Technical Coordinating Group for Aircraft Survivability (JTCG/AS), Falcon R&D has recently completed a test and modeling program to study fires in interior regions adjacent to fuel tanks (i.e., "external" fuel tank fires) caused by incendiary bullets and high energy lasers. Of particular importance was the influence upon fire sustainment of airflow in and about the damage hole in the exterior skin of the aircraft made by the projectile or the laser.

The approach to this program was strongly influenced by prior work. Particularly relevant were gunfire tests of replica and actual aircraft fuel tanks with exterior airflow. These tests were somewhat limited in their effectiveness by their expense and problems with test repeatability. Prior work also indicated that simulation of the turbulent boundary layer adjacent to the exterior of the aircraft may be important for proper interaction with skin damage holes.

Some fundamental aspects of this study were:

1. The study consisted of a parallel modeling and test effort. The model served to assist in the design of the test program. Test results were used to refine the model. The results of the test program can most confidently be extended beyond the conditions simulated by use of the refined model.
2. The test program isolated and systematically assessed the influence of parameters deemed crucial to the sustainment and extinction of fuel fires in flight.

AFAPL Contract

3. The terminal effects of incendiary bullets and high energy lasers were pyrotechnically simulated. This provided a much higher number of tests for the funds available. Also, the projectile terminal effects were more precisely controlled and repeated, compared with the unavoidable variations in functioning with actual incendiary bullets.

4. The experiments were essentially full-scale in terms of the volume and spacing between the tank wall and simulated aircraft skin, the size and energy of the simulated threat effects, and the velocities and flow rates of interior and exterior airflow (300 ft/sec). Fuel spray and leakage were realistically simulated, using representative spray quantities and leakage flow rates of JP-4 fuel.

5. The steady-state aerodynamic conditions and affected transient (flash) and sustained fires were measured and observed in far greater detail than in prior experimental programs.

The "External Fire Model" applicable to incendiary projectiles was developed primarily by Dr. William A. Sirignano of Princeton University, who served as a consultant to Falcon R&D for this task.<sup>1</sup> The fundamental approach was to treat the hazardous space between the fuel tank wall and the aircraft skin as a well-stirred region. Airflow into this region from the interior of the aircraft and through the hole in the skin is modeled, as well as flow out of this region into the downstream interior of the aircraft. Reversals of airflow direction at these inlets/outlets with combustion-induced pressure fluctuations are also accommodated by the model. Since the experiments showed that the airflow can cause a vortex motion which can affect vaporization rates, a vortex velocity may be input into the model.

Vaporization from projectile-induced spray, continuous leakage from the damaged tank, and a pool of fuel in the bottom of the bay are modeled. The model assumes a polydisperse but discrete spray is known. Various groupings of droplet size are considered, and different sprays are produced in pulses at prescribed time intervals.

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<sup>1</sup> Sirignano, W. A.; Mahood, L.; Hutchinson, D.E.; *External Fire Model for Fuel System Vulnerability Assessment; User and Analyst Manual*, Technical Report JTCG/AS \_\_\_, Air Force Aero Propulsion Laboratory, WPAFB, OH.; April, 1978.

The energy release and the pressure are determined through a large coupled system of equations which include the continuity, energy, fuel vapor species, and oxygen species equations for the gas phase. Also included are droplet continuity, momentum, and radius equations. The model is operated over a period of time sufficient to determine if the combustion has quickly subsided--giving tolerable damage to the aircraft--or rather that combustion is sustained and an aircraft "kill" will result.

The experimental program consisted of 135 tests. The results are summarized below in terms of the particular aircraft configurations to which they apply.

**Closed Void Spaces** - represent relatively well sealed regions adjacent to the fuel tanks, where the only airflow is through the damage hole. For all spaces tested, the probability of sustained fire was zero. This applies to aircraft skin-to-tank-wall spacings of 1, 4, 6, and 10 inches (0.3 to 3 cubic feet volume).

These and other tests revealed that a high velocity jet of air entered the void space through the damage hole. The velocity of this jet increased with increasing slipstream static pressure (varied over a range of -6.5 to 57 pounds per square foot). A relatively large vortex was also observed within the void space. Its axis was horizontal and its apex was at the upstream portion of the damage hole--where air outflow was obviously occurring.

**Open Void Spaces** - represent relatively unblocked communication between the void space and the rest of the interior of the aircraft. The probability of sustained fire in open void spaces was unity. The sustained fires were primarily associated with the pool of fuel accumulating in the bottom of the void space due to continuous leakage from the tank.

**Ventilated Void Spaces** - represent semi-enclosed spaces with forced air ventilation prior to skin perforation by the threat. Sustained fire probability was dependent upon the rate and configuration of the simulated airflow from the interior of the aircraft--which supplemented the ventilation through the damage hole.

For high interior ventilation rates (to 465 cfm), sustained fires resulted. The fire was mainly associated with the spray developed from the airflow over the leaking fuel stream.

For a 4-inch skin-to-tank wall spacing (1.25 cubic feet), an interior ventilation rate of 21 cfm was the lower limit for sustained fires with relatively diffuse air inflow. For a single inlet orifice, the minimum rate for sustained burning was 48 cfm. Below these minima, only transient (flash) fires resulted.

Comparisons with tests with the damage hole blocked indicated that a minimum total airflow rate through the void space of 48 cfm was necessary for sustained fire with good mixing (diffuse interior air inflow), and 66 cfm for a single orifice for interior air inflow.

For a 6-inch skin-to-tank-wall spacing (1.86 cubic feet), the combined flow rate of 132 cfm was necessary for sustained fire for a single orifice for interior air inflow.

These tests demonstrated that interior ventilation flow conditions that have commonly been characterized only by the number of "air changes per minute" are not sufficient applied to void spaces of the sizes investigated in this program. The configuration of that interior airflow must be at least approximately defined for a confident sustained fire hazard assessment.

MULTIPLE IGNITION, COMBUSTION AND QUENCHING OF HYDROCARBON  
FUEL SPRAYS AND HIGH TEMPERATURE CATALYTIC COMBUSTION

(AFOSR-76-3052B)

William A. Sirignano and Howard S. Homan

Mechanical and Aerospace Engineering Department  
Princeton University  
Princeton, New Jersey 08540

Ignition of combustible fuel-air mixtures by burning metal particles presents a fire hazard. Aircraft fires can be started in this way when projectiles penetrate fuel tanks. Fuel spraying through the punctures into the dry bay or splashing into the ullage yields a combustible mixture; the burning metal particles are abraded from the aircraft structure or originate from projectiles with metallized explosives. Similar fire hazards exist in rooms with combustible environments and in mines where electrical equipment or abrasion can supply burning metal particles. The physical situation relevant to aircraft involves a cloud of hot and burning metal particles passing through a mixture of fuel vapor, fuel droplets, and air near damaged fuel tanks. This investigation is the first step toward understanding the fire hazard for this situation. The important variables governing ignition are particle size and type, fuel/air mixture ratio, pressure, and initial particle temperature. It is desired to determine experimentally the envelope of these variables, in which the combustible gas ignites, and to predict theoretically this envelope.

Experiments to determine the minimum size of burning aluminum particles needed to ignite  $\text{CH}_4/\text{Air}$  mixtures will be discussed. The aluminum particle, about  $100\text{ }\mu\text{m}$  in diameter, is suspended on a glass filament in a methane/air mixture. The mixture is in a closed vessel with Plexiglas windows so the metal particle can be ignited by a pulse from a Nd:Glass laser. Measurements are made of the timing and order of events that follow the laser pulse. A Sundstrand Model 601B quartz pressure transducer will be flush-mounted in the wall of the vessel. An oscilloscope is used to record the pressure versus time in the vessel. The record will show if the  $\text{CH}_4/\text{Air}$  mixture is ignited by the aluminum particle. Photos show whether the metal particle ignited and burned. The effect of the laser pulse on the process of ignition of the combustible gas by the burning particle is minimized by using the minimum laser flux required to ignite the particle. The minimum particle mass necessary for ignition of the gas is expected to be a strong function of  $\text{CH}_4/\text{Air}$  equivalence ratio. The data are used to argue that local oxygen depletion by the burning particle is large enough to have a significant effect on gas phase reactions that precede the formation of a flame in the gas. The argument involves

a comparison of energy liberated by burning the particle with minimum spark ignition energies for the combustible gas.

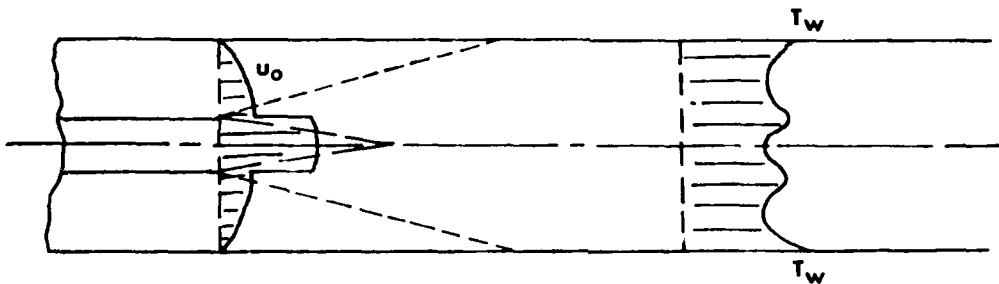
With regard to theory, a description of the equations and assumptions for the numerical determination of the temporal and spacial distribution of temperature and species in a combustible gas will be presented. The case considered is the ignition of a quiescent combustible gas by a stationary hot, inert, spherical particle. (This is a first step toward a model which will include the complications of gas phase kinetics and chemically active particles.) The range of initial conditions that result in a flame propagating away from the particle are sought. The initial conditions are particle temperature, fuel-air ratio, and pressure of the combustible gas. Other important parameters are the particle radius and specific heat. Results of the model indicate that a non-burning aluminum particle formed by abrasion must have a diameter larger than 2 mm to cause ignition. This is because the temperature of the abraded particle can be no higher than its melting temperature.

# IGNITION AND COMBUSTION IN A LAMINAR TUBE FLOW WITH HOT TUBE SURFACE

AFOSR-78-3538\*

Thomas B.C. Shen  
Southeastern Massachusetts University  
North Dartmouth, Mass 02747

This presentation reports some results from the study of a tubular flow problem. The following diagram shows the sketch. Essentially, it consists of two coaxial tubes. A fuel gas jet flows out of the inner tube and joins the oxygen-containing outer tube flow. As the two flows



move downstream, they diffuse to each other to form mixture of fuel gas and oxygen( and some inert gaseous ingredient) of different concentrations. At any temperature level, a corresponding degree of chemical reaction ( according to Arrhenius law) occurs. At appropriate temperature levels, ignition and then combustion occur. For analysis, it is a 2-dimensional, cylindrical coordinates, steady, compressible, laminar, chemically reactive tubular flow problem, in which convection, diffusion, heat transfer and chemical reaction processes are considered. In practice, this analysis models many experimental arrangements for combustible gaseous flammability tests. Also, the ignition mechanism may help to explain the starting of the

\*All calculations are done in Aitken Computation Laboratory, Harvard University, Cambridge, Mass, 02138



flame near the fuel gas ports is a combustor or, in general, near the nozzle of any laminar fuel gas jet in flowing gaseous environment. This work starts from the beginning of this year (1978) on a part time basis. This analysis is still in progress.

The current analysis( up to now ) contains essentially the solution of a set of five simultaneous partial differential equations, i.e., the continuity equation, the flow direction momentum equation, the energy equation and two specie (fuel gas and oxydizer ) continuity equations. Fluid is compressible, ideal. Pressure along the tube direction varies and can be calculated from conservation principle. All the properties are constant. Numerical method is used in calculating the solution. Now numerical algorithms are designed to facilitate the calculation convergence rate.

To this phenomenon, the controlling parameters in dimensionless forms are the Reynold's number, the Prandtl number, the Schmidt number (or the Lewis number), tube wall temperature, initial pressure level, chemical reaction time, chemical reaction heat, and the activation energy, together with the specified initial conditions of velocity, temperature, fuel concentration and oxygen concentration.

Solution provides all the local profiles, both in radial and flow directions. Local wall heat transfer coefficient, expressed in  $Nu_x$  form, is calculated. Ignition, defined as the first occurrence of the maximum temperature on a radial temperature profile along the flow direction, can be identified.

From the preliminary results, following several features of

the solution are observed:

- (1) First ignition occurs downstream of the inner tube exit in line with the inner tube wall. The distance between the inner tube exit and the first ignition varies with Reynolds number. The larger is the Reynolds number, the longer is the distance. The distance may reach fraction of tube diameter as Reynolds number approaches its upper limit of laminar flow ( 2300). No blow-off limit observed within the whole Reynolds number range for the cases studied. From the results, two ignition fronts are observed. One, the major one inclines towards the wall; the other, a minor one, inclines towards the center. The growth rate of the width between the two ignition fronts decrease with the Reynolds number.
- (2) For inert gas flow ( without considering the chemical reaction ), the wall heat transfer coefficient decreases along the tube direction, decreases with the tube wall temperature, decreases with the jet velocity.

At the present moment, more ignition study are carried out. The extension of this study to turbulent regime appears a logic next step activities, which will be started in the near future again on part time basis.

## Ignition of a Liquid Fuel Under High Intensity Radiation

Takashi Kashiwagi

Center for Fire Research  
National Bureau of Standards  
Washington, D.C. 20234

Laser technology has been rapidly advancing in the last two decades. Power outputs of modern lasers have increased significantly and these lasers can be used as tactical weapons. A high power laser weapon can ignite aircraft fuel through fuel tank penetration and can cause fire or explosion of the aircraft. The objective of this study is to obtain a fundamental understanding of physical and chemical mechanisms of the ignition of liquid fuels under high intensity radiation, thus enabling future improvements in aircraft survivability from fire and explosion threats.

Since the radiative ignition of flammable liquids is hardly known, an experimental study is being conducted to clarify the key mechanisms of ignition. The following experiments were conducted using a CO<sub>2</sub> laser and n-decane as the flammable liquid. The first was to take high speed photographs of the motion of the decane surface after its exposure to the incident laser beam and of the onset of ignition in the gas phase. Results would reveal the behavior of the decane surface during the heating period and the location of the first ignition and subsequent flame spread. The second was to find the effects of incident angle of the laser beam with respect to the decane surface on ignition delay time. The third was to measure the extinction coefficient of liquid decane at laser wavelengths to find how deep the laser beam penetrated into the decane.

High speed motion pictures show clearly the motion of the decane surface prior to ignition. When the laser beam irradiated the decane surface, a small amount of splash of decane was observed followed by small waves moving radially outward. This behavior appears similar to that seen when a stone is thrown into a pond. Boiling of the decane was vigorous accompanied with bursting sounds similar to that heard when water droplets would fall onto a high temperature plate. The onset of ignition was observed in the gas phase far from the decane surface. On reducing the incident angle of the laser beam to the decane surface, the onset of ignition occurred further away from the plume center line, i.e., toward the edge of the plume. Rapid flame spread along the plume of the decane vapor was observed immediately after ignition. Color photographs showed that bright yellow color of a small rod shape at the location where the incident laser beam interacted with the plume of the decane vapor. This was much

brighter color than the rest of flame and it remained until the laser beam was turned off. From this observation, it is considered that the absorption of the laser beam by the decane vapor is the key heating process of the gas phase prior to ignition. This was confirmed by the ignition of vapor from decane heated by an electrical hot plate by passing the laser beam through the vapor parallel to but above the liquid decane surface. Therefore, the ignition mechanism of decane by high intensity radiation is the absorption of the incident radiant energy by its vapor plume.

The relationship between the ignition delay time and the incident flux were studied with various incident angles of the laser beam at 30°, 45°, 60°, 75° and 90°. Below 2500 W/cm<sup>2</sup>, ignition delay time increases significantly with a decrease in flux. There is a peculiar trend where ignition delay time tends to increase slightly with incident radiant flux in the range of high flux. This was observed at all incident angles studied in this work. It is not clear what mechanism causes this trend. It is observed that the minimum incident radiant flux for ignition,  $I_{\min}$ , increases with a decrease in the incident angle. At  $\theta = 75^\circ$  and 90°,  $I_{\min} \approx 1000$  W/cm<sup>2</sup>, but at  $\theta = 60^\circ$ ,  $I_{\min} \approx 1400$  W/cm<sup>2</sup>, at  $\theta = 45^\circ$ ,  $I_{\min} \approx 1800$  W/cm<sup>2</sup> and at  $\theta = 30^\circ$ ,  $I_{\min} \approx 2000$  W/cm<sup>2</sup>.

The relationships between the ignition delay time and the incident flux do not differ from each other significantly at  $\theta = 60^\circ$ , 75° and 90° except near the ignition boundary. However, the relationships at  $\theta = 30^\circ$  and 45° differ significantly from other angles. Ignition delay time becomes longer over a wide range of the incident radiant flux.

To obtain the extinction coefficient of liquid decane, linear absorbance was measured from wave number 1100 to 800 cm<sup>-1</sup> by a Perkin-Elmer Model 180 Infrared Photometer using a variable length cell. It was found that the absorbance of the decane was sensitive to the wave number near the CO<sub>2</sub> laser lines. Therefore, the bulk extinction coefficient of decane was calculated from the spectra of the fine rotational structure of the CO<sub>2</sub> laser and the linear absorbance. Since the rotational line of the laser is much narrower than absorption bands of decane, the laser line was considered to be delta function in the integration along the wave number. The calculated extinction coefficient of decane is 17 cm<sup>-1</sup>. This is much smaller than for many solids. For example, about 90 cm<sup>-1</sup> of solid polystyrene. Therefore, the laser beam penetrates into decane and heats a larger volume than polystyrene. This is one of the reasons why decane requires higher incident flux for ignition and its ignition delay time is longer than polystyrene.

Ignition of Fuel Sprays by Hot Surfaces  
and Stabilization of Aircraft Fires  
(Contract/Grant AFOSR-77-3446)

J.G. Skifstad and A.H. Lefebvre

School of Mechanical Engineering  
Purdue University  
West Lafayette, Indiana

The research in this project is concerned with two general topics related to aircraft fire safety: (1) the ignition of fuel sprays by hot surfaces and (2) the stabilization of both external and internal aircraft fires. Existing data are insufficient to enable assessment of aircraft fire hazards; it is the purpose of this research to obtain fundamental data and to develop appropriate theoretical descriptions of the phenomena for hazard assessment purposes.

Ignition of fuel sprays by hot surfaces is being investigated by injection of a fuel spray into an airflow of known properties passing through a heated pipe section. The influence of spray, airflow, and surface properties are to be investigated for each fuel considered. The experimental facility for this purpose was designed to meet rather stringent conditions. A discussion of the design conditions and a description of the facility are presented. The instrumentation and preliminary measurements are discussed, including performance of the facility and preliminary ignition experiments.

Stabilization of aircraft fires by large-scale flameholders is to be investigated in a combustion tunnel initially with V-type and L-type gutters, using the water injection method developed by Lefebvre. A review of the technical aspects of the problem is presented, outlining the data required and the range of conditions to be investigated. The combustion tunnel in which this part of the research is to be conducted is described, along with plans for the coming year, which include as well exploratory investigations in the combustion tunnel related to the stabilization of void-space fires.

IGNITION, COMBUSTION, DETONATION, and  
QUENCHING OF REACTIVE MIXTURES

R. Edse

Department of Aeronautical and Astronautical  
Engineering, The Ohio STATE UNIVERSITY

Knowledge and data resulting from this research will be of help to engineers at the U. S. Air Force to design more efficient power plants for aircraft and high speed missiles, effective flame arrestors for minimizing the hazards of fuel tank fires of aircraft, and systems providing high pressure shock waves from explosions of unconfined fuel-air mixtures.

Although flame arrestors may be developed by lengthy and costly trial and error procedures, more effective devices can be constructed on the basis of a fundamental understanding of the flame quenching process. For this reason a comprehensive experimental study of the flame quenching process was undertaken. A burner tube having a rectangular cross section with a length to width ratio of approximately 200 has been used for determining the quenching distances of various fuel oxidizer mixtures by squeezing the flames between two movable plates which are mounted parallel to the long side of the burner. For laminar flames the measured quenching distances were found to be independent of the linear speed of the unburned gas and the geometry of the burner tube but dependent on the type and nature of the quenching surface, the thermal conductivity, diffusion rates, and specific heats of the unburned gas. Furthermore, flame temperature, flame propagation rates and the composition of the combustible gas mixture had a great influence on the quenching process. Spectrographic analyses of unquenched and partially quenched flames revealed that several of the active species and free radicals normally present in unquenched flames are not observed in partially quenched flames. This observation indicates that the quenching process involves a significant change of the reaction mechanism of the combustion process. Furthermore extremely high rotational temperatures have been observed in partially quenched flames whose translational temperatures (measured by thermocouples) were actually much lower than those of the corresponding unquenched flames. This finding clearly indicates that the quenching process produces highly non-equilibrium states in the combustion gases. A simple one-dimensional model of the flame has been used to develop a theoretical equation for predicting quenching distances of flames of various fuel-oxidizer mixtures. The quenching distances derived from this equation agree reasonably well with those obtained by experimental measurements.

For a better understanding of the mechanism of transition from deflagration to detonation a series of experiments is being carried out to determine the induction distances in various fuel-oxidizer mixtures at different densities and with inert gas additives of different molecular mass. Results of these studies are of great importance in treating the phenomenon of combustion instability, for the formation of strong shock waves in unconfined fuel-air mixtures, and the design of flame arrestors.

BASIC INSTABILITY MECHANISMS  
IN CHEMICALLY REACTING SUBSONIC AND SUPERSONIC FLOWS  
(Grant AFOSR - 74 - 2619)

T. Y. Toong

Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

This research on instability mechanisms involved in the mutual influence among sound, entropy, and vorticity modes in chemically reacting subsonic and supersonic flows will aid in the design and development of practical combustors for advanced air-breathing and hybrid engines, for MHD generators and chemical lasers. Further, it will also provide the fundamental information needed to solve many practical problems related to noise pollution and unconfined explosions.

One basic mechanism that plays an important role in triggering and sustaining instabilities in chemically reacting flows, such as that related to combustion instabilities, detonation wave structure, turbulence spectra in reacting flows, etc., is due to the coupling between chemical kinetics and gas dynamics. Such coupling could lead to wave interactions which would sustain the instability structures observed in a number of problems<sup>1</sup>.

During the initial phase of the development of the instabilities, the amplitudes of the waves involved are usually small and the wave-kinetic interactions can be treated in a linear acoustic analysis (despite non-linear chemical kinetics through temperature and concentration dependence). Considerable insight on such acoustic-kinetic interactions has been obtained in several theoretical studies<sup>1-6</sup>. Furthermore, predictions in the quasi-steady regime, when the ratio  $\Omega$  of the characteristic chemical time to the acoustic period is large, are found to agree well with the experimental results in  $H_2-Cl_2$  systems<sup>7,8</sup>. When the ratio  $\Omega$  becomes smaller (due to either faster reaction rates or lower acoustic frequencies), theory<sup>2,5,6</sup> predicts larger chemical effects. The first part of this paper will present experimental results to substantiate such theoretical predictions.

During the later phase of the development of the instabilities, the wave amplitudes become large and the accompanying non-linear effects may become important. The second part of this paper will discuss such non-linear interactions by examining the amplification and dispersion of weak shocks propagating in a reacting mixture.



### Acoustic-Kinetic Interactions

The propagation of acoustic waves in a homogeneous mixture of hydrogen and chlorine (diluted with argon) was examined in a 5.5m long, 8-cm diameter Pyrex tube, surrounded by dc fluorescent black-light lamps. The photochemical reaction between hydrogen and chlorine was initiated by ultraviolet radiation incident onto the premixed, homogeneous reactive mixture. The overall reaction rate was measured by monitoring the quantity of uv light absorbed by molecular chlorine with a photomultiplier equipped with a narrow-band filter, and the mean temperature of the gas by means of tungsten-wire resistance thermometers. The average chlorine consumption rate and the corresponding mean temperature history were thus available for each experiment.

Two different wave configurations were employed in this investigation. In one configuration, sound waves were generated at one end of the reaction tube by means of a piston, actuated by a mechanical shaker. A pulse generator-function generator-power amplifier combination was used to generate a 2-cycle burst of a given frequency which propagates down the tube. Sound pressure was monitored at various stations along the tube by means of several miniature condenser microphones. The incident burst reflected back and forth at both ends of the tube and as a result, one was able to examine a specific 2-cycle burst during a time interval as long as 1/2 sec, before its amplitude reached the noise level due to dissipation. This mode of operation was used for high acoustic frequencies (above 300 Hz).

In the other configuration, the piston-shaker was used to establish first a standing wave in the reaction tube at one of its resonant frequencies. Once the wave attained its maximum amplitude, the piston-shaker was turned off and the reaction initiated. The behavior of the resulting wave was then monitored by microphones and compared with that in a non-reacting mixture. This mode of operation was used at lower acoustic frequencies (32 and 64 Hz).

The approach taken in this investigation is to identify and study the effects of non-equilibrium reaction on sound propagation by comparing the changes in pressure amplitudes before and during chemical reaction for given initial mixture composition, pressure and acoustic frequency. In these experiments, amplification of the sound pressure fluctuations have been consistently observed. At high values of the dimensionless frequency  $\Omega$ , the measured amplification rates obtained with both wave configurations agree with the theoretical predictions for the quasi-steady regime; a result which demonstrates that the effect due to acoustic-kinetic coupling is essentially the same for a travelling wave (sound burst) and a standing wave (two oppositely travelling waves) at the same value  $\Omega$ , despite different mixture compositions and acoustic frequencies. The measured amplification rates are also found to be independent of the initial sound pressure level of the standing waves, thus

confirming the linear approximations employed in the theoretical predictions.

The values of  $\Omega$  attained in both configurations, however, were found to fall in the quasi-steady regime, in spite of the low acoustic frequencies used in the standing-wave experiments. Also, at high reaction rates, standing waves, whose sound pressure levels are much higher than those generated by the piston-shaker, are triggered. This limits the observations to the initial phase of the reaction history, where reaction rates are still low.

To overcome this difficulty, a third configuration was employed. A shock-generating system, which consisted of a flat solenoid in contact with a thin metallic diaphragm, was used to generate planar weak shocks of controlled strengths and widths, when a high-voltage capacitor discharged through the solenoid. The weak-shock amplitudes were high enough above the noise level, which made it possible to employ much higher reaction rates. On the other hand, the amplitudes were low enough in order not to introduce additional non-linear kinetic terms. The shock examined consisted of a typical N-wave with a steep leading front. However, due to successively decaying rebounds of the diaphragm, the shock was followed by weaker trailing waves of lower amplitudes and frequencies.

Experiments show that the shock strengths are amplified due to chemical reaction. However, the trailing waves show much larger amplification rates. When compared with quasi-steady predictions, the leading shocks show good agreement, while the trailing waves display amplification rates that are much higher than the predicted values.

The characteristic frequencies of the various waves were used to estimate their respective non-dimensional values,  $\Omega$ . In the case of the leading shocks, the values of  $\Omega$  were found to fall in the quasi-steady limit, a result which confirms the good agreement with the predictions. The values of  $\Omega$  for the trailing waves were found to fall in the non-quasi-steady limit, where stronger acoustic-kinetic interactions are expected, as inferred from the theoretical predictions<sup>5</sup>. These findings are in agreement with the experimental observations.

#### Shock-Kinetic Interactions

In order to study the non-linear wave-kinetic interactions, the amplitudes and structure of weak shocks propagating in hydrogen-chlorine-argon mixtures are examined in another pyrex tube, 2-m long and 8-cm in diameter. A shock-generating system, which consisted of a short high-pressure driver section attached to one end of the tube, was used to generate weak  $(1/2)N$  shock pulses of controlled strengths and widths, when the separating diaphragm is ruptured. The travelling shocks were monitored by sensitive pressure transducers as they reflected back and forth at both ends of the reaction tube. The reaction histories were monitored by means of resistance

thermometers and a photomultiplier.

Preliminary experiments at shock Mach numbers 1.15 show that, despite the high loss rate at the shock front, the waves are sustained by chemical reaction. For high reaction rates, the waves can develop from a successively decaying  $(1/2)N$  wave into a rapidly expanding shock pulse. It is believed that, according to the kinetic parameters for the  $H_2-Cl_2$  reaction, non-linear kinetic effects would be expected.

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CATALYTIC COMBUSTORS FOR FUTURE AIRCRAFT  
GAS TURBINE ENGINES

Dr. Larry A. Diehl

Combustion Fundamentals Section  
NASA Lewis Research Center  
Cleveland, Ohio

With catalytic combustion, it is possible to obtain both high combustion efficiency and ultra-low  $\text{NO}_x$  emissions at the same time. A developed catalytic combustion system can be shown to have advantages in terms of system performance, hot section component life, and combustion stability. A jointly funded effort between NASA and the Air Force is being performed under contract in pursuit of these benefits.

The purpose of this program is to evaluate the feasibility of employing catalytic combustion technology in aircraft gas turbine engines. The system performance must be maintained or improved compared with current engines. The successful adaptation of catalytic combustor technology to practical combustion systems will require advancements in the following principal areas: (1) minimizing catalyst-bed pressure loss; (2) maintaining catalyst-bed combustion efficiency at an acceptable level; (3) increasing catalyst-bed long-term operating temperature levels; (4) eliminating autoignition and flashback; (5) achieving and maintaining fuel-air premixing quality. Fundamental studies of autoignition and flashback phenomena and fuel-air mixture preparation have been underway as part of a major NASA effort in premixed/prevaporized combustion technology. Those studies apply equally as well to catalytic combustion systems.

The catalytic combustion program will be performed in three phases: Phase I is a study to design and analytically evaluate a number of potential combustor candidates; in Phase II, promising combustor designs will undergo a series of designs, tests, design modifications, and retests in a combustor sector rig; further development and testing in either a sector or full-annular combustor rig will take place in Phase III with one or two catalytic combustor designs selected for further refinement toward aircraft application.

In the Phase I study, currently underway, the following goals are established for the combustor designs: The emission goals include a  $\text{NO}_x$  emission index of less than one at

subsonic cruise and pollutant emission values sufficiently low over the EPA landing-takeoff cycle to meet EPA standard values. The performance goals include high combustion efficiency over all operating conditions and a pressure loss for the combustor system of 5% or less. In addition to these goals, combustor durability, reliability, size and weight penalties, safety considerations and complexity of design will be considered in the combustor evaluations.

The Phase I contract activities with General Electric and Pratt & Whitney are now about 70% complete. Detailed analysis of six potential combustor designs suggested by each contractor have been completed. The two most promising designs identified in each study will undergo additional analysis and will involve the generation of preliminary design drawings. Results of the studies will include recommendations either for follow-on combustor research or for further work on certain aspects of catalytic combustors before development is practical. Using these Phase I results, a decision will be made by the government as to whether or not to proceed with the program into Phases II and III.

APPLICATION OF CATALYTIC FLAME STABILIZATION  
FOR AIRCRAFT AFTERBURNERS  
AFAPL/In House

Leonard C. Angello

Department of the Air Force  
Air Force Aero Propulsion Laboratory (AFSC)  
Wright-Patterson AFB, OH 45433

Catalytic flame stabilization encompasses the use of a porous catalytic surface to initiate, stabilize, and provide a continuous pilot for flame propagation. A current program at the Air Force Aero Propulsion Laboratory (AFAPL) is considering the use of catalytic material in the afterburner of a jet engine. The principal goal of this program is to employ catalytic flame stabilization in such a manner that system performance gains result.

This paper develops the application of catalytic flame stabilization to aircraft afterburners. The concept will be contrasted with conventional flameholding, indicating those areas of benefit. An AFAPL program to test concept feasibility using a JG5-5 engine will be outlined, including a simplified modeling effort used to guide the test hardware design. The results of a system performance trade-off study indicating potential limitations on the afterburner application will also be presented.

# HIGH TEMPERATURE CATALYTIC COMBUSTION

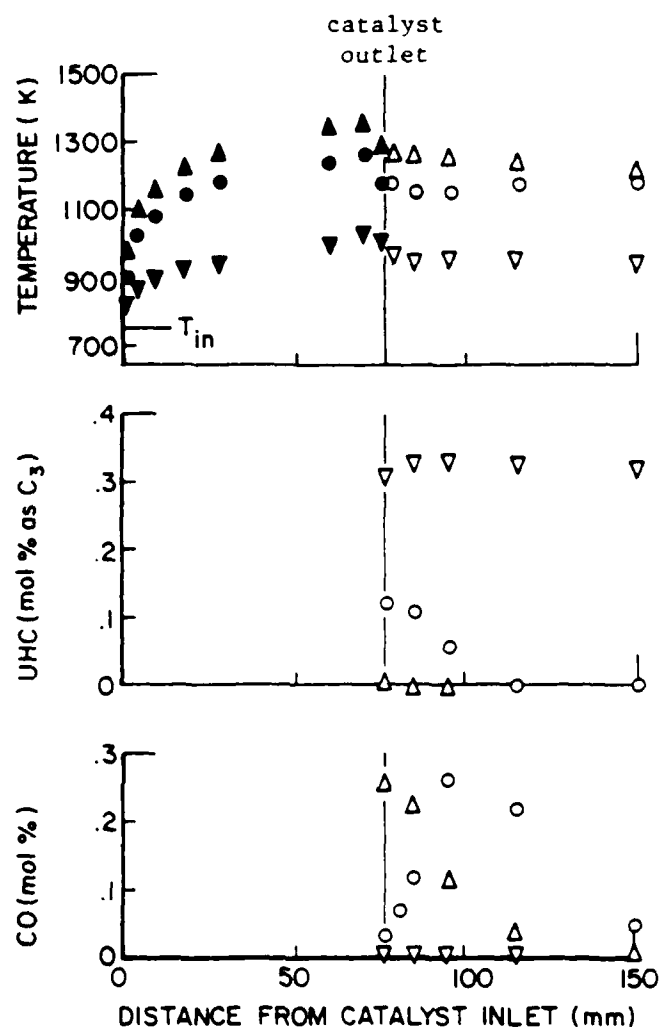
P. M. Walsh, C. Bruno, D. A. Santavicca,  
B. Kim, and F. V. Bracco

Department of Mechanical and Aerospace Engineering  
Princeton University  
Princeton, NJ 08540

The possibility of improving jet engine emissions and performance with monolithic combustion catalysts is being investigated. The goal of the research program is to understand the relative importance of the controlling sub-processes (surface reactions, gas phase reactions, and transport processes) and to develop a two-dimensional model of combustion in catalytic channels which can be used in optimization studies. Experimental measurements of substrate temperature and gas composition, pressure, and temperature inside and downstream of the catalyst will test the usefulness of the model in predicting the dependence of combustor performance on inlet gas conditions and catalyst properties.

The present test rig uses a 25x25x76 mm catalyst sample. Gaseous fuel is injected through a grid of 25 holes and mixed by baffles to achieve  $\pm 1\%$  composition uniformity across the inlet gas stream. The test section is insulated to maintain temperature uniformity of  $\pm 1\%$ . Gas velocity is uniform within  $\pm 6\%$  over the center half of the width of the test section. Substrate temperatures are measured with thermocouples embedded in sealed monolith cells. Gas samples are extracted through a water-cooled probe which contains a thermocouple for simultaneous gas temperature measurements.

Lean combustion of carbon monoxide and propane in platinum/alumina/cordierite catalysts is being studied at atmospheric pressure and gas velocities of 5-30 m/s. The dependences of substrate temperature, gas temperature, and gas composition on inlet temperature, reference velocity, and equivalence ratio have been investigated. The data in the figure show the variation of emissions with equivalence ratio for propane/air combustion. Homogeneous reactions in the exhaust are observed only at the higher equivalence ratios. Broader interpretation of the variation in exhaust composition with inlet conditions awaits completion of the development of the numerical model.



substrate	gas	equivalence ratio
▼	▽	0.20
●	○	0.25
▲	△	0.28

Substrate temperature, exhaust temperature, unburned hydrocarbon, and CO emission at three equivalence ratios for propane combustion in a Pt/Al<sub>2</sub>O<sub>3</sub>/Cordierite catalyst.

Inlet pressure: 110 kPa  
 Inlet temperature: 750 K  
 Reference velocity: 9 m/s



CONTRIBUTION OF SURFACE CATALYSIS AND  
GAS PHASE REACTION TO CATALYTIC COMBUSTOR PERFORMANCE

Principal Investigators: C. M. Ablow, B. J. Wood, and H. Wise

SRI International  
Menlo Park, California 94025

In order to be able to predict the performance characteristics of a catalytic combustor it is important to have a quantitative understanding of the contributions of surface-catalyzed and gas-phase reactions over a range of operating conditions. In the first phase of our investigation we have developed a theoretical model of the steady, reactive flow of a fuel/air mixture passing through a catalytically active duct of a honeycomb monolith. In this model we assume plug flow at constant pressure and take average constant values for the transport parameters. Axial conduction of heat in the gas and in the duct wall is neglected in comparison with convection in the gas and radial conduction through the wall to the surroundings, assumptions that differ from those of a similar model.<sup>1</sup> The model uses global reaction kinetics with first-order dependence of the reaction rate on the fuel concentration in the presence of excess air. These kinetic parameters are obtained from separate studies of the platinum-catalyzed oxidation of various hydrocarbon fuels at concentrations and catalyst temperatures in the same range as employed in catalytic monolith combustion.<sup>2</sup>

The theoretical model is developed in nondimensional form so that governing parameters can be identified. These include the reduced activation energies and Damkohler numbers for the gas phase and catalyst wall reactions, the Stanton number for heat transfer between the gas and duct wall, the Lewis number ratio of gas transport coefficients, and the ratio of the inlet gas temperature to the theoretical temperature rise under adiabatic conditions.

In the adiabatic case where no heat is exchanged through the duct walls, an analytic solution has been obtained relating the temperatures and concentrations at the wall and in the stream that can exist at any cross section of the duct. From this phase space solution one can readily obtain parameter ranges where the wall reaction is controlled by surface kinetics or by diffusion, where the gas phase reaction makes a contribution, or where multiple responses can occur.

Contract No. F49620-77-C-0123

Ducts in the interior of the monolith are well modelled by the adiabatic case. Ducts on the periphery of the monolith exchange heat with their surroundings. In this nonadiabatic case the temperatures and concentrations are so coupled to distance down the duct that the differential equations of the model generally require numerical solution. Analytic solutions can be obtained in the limiting case of wall reaction controlled by diffusion and negligible gas phase reaction.

The theoretical analyses has been applied to two sets of experimental measurements of Pt catalyzed combustion. In one set, carried out in our laboratory, the conditions for transition from kinetic to diffusive control were determined for propane/air and propane/oxygen/helium mixtures. In the other set, measurements were made of diffusion-controlled reactions in propylene/oxygen/nitrogen and hydrogen/oxygen/nitrogen mixtures.<sup>3</sup> Satisfactory agreement between the experimental observations and the predictions of the theoretical model were obtained in both cases. In particular for the  $H_2/O_2/N_2$  system the model confirms that the small Lewis number ( $Le < 1$ ) is the cause for a wall temperature maximum in excess of the adiabatic reaction temperature.

The agreement between theory and experiment suggests the utility of the present model in the engineering design of catalytic combustors over a wide range of operating conditions.

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## INTERFACIAL CHEMICAL REACTIONS IN FLOW SYSTEMS

(Contract F 49620-76-C-0020)

Daniel E. Rosner

High Temperature Chemical Reaction Engineering Laboratory  
Yale University, New Haven, CT 06520

Energy and mass transfer processes dictate the useful lifetime of surfaces in external and internal aerodynamic systems, particularly in the presence of simultaneous chemical reaction. In this program we are combining experiments using low pressure flow reactors with convective diffusion theory to gain an understanding of the important phenomena and rate constants useful for future design/optimization purposes. Most of our current work can be grouped into the three areas: 1) energy partitioning in heterogeneous chemical reactions, 2) convective diffusion in multicomponent nonisothermal systems; and 3) oxidative vaporization of refractory solids. Details beyond those mentioned below can be found in the references cited.

1. Energy Partitioning in Heterogeneous Chemical Reactions<sup>1,2</sup>

When highly exoergic reactions occur at surfaces how does the energy release partition between the surface and the desorbed product molecules? Where do the excited product molecules quench, releasing their energy? These questions are being studied for prototype systems, with experimental emphasis on the surface-catalyzed association of atomic nitrogen and the surface-catalyzed decomposition of hydrazine vapor. Using a novel coaxial filament flow reactor (CFFR) we have recently completed calorimetric studies<sup>2</sup> of N-atom association on the metals Pt, W, Ir, Rh, Pd, W, Re, Co over a wide temperature range (up to 2600K for W and Re) we find that incomplete energy deposition can be appreciable (> 80% of the equilibrium energy of reaction escapes) and can occur either at "low" temperatures (eg. the N/W and N/Re systems) or at high temperatures (eg. N/Pt and N/Ir). A Langmuir-type mass-action law analysis, combined with simple postulates (ie, Rideal-produced molecules depart excited whereas Langmuir-Hinshelwood-produced molecules do not) permits a semi-quantitative understanding of our observed chemical energy accommodation coefficients ( $\beta$  - values) for the N/W, N/Re systems in terms of sticking coefficients, adatom binding energies and an elementary Rideal reaction probability. The experimental technique is now being extended to determine physical and chemical energy accommodation coefficients for the  $N_2H_4$ /Ir and  $N_2H_4$ /W systems. When such reactions occur in porous catalytic media secondary quenching events influence the energy deposition behavior, as will be illustrated by mathematical models of chemical energy release in single pores and porous catalytic slabs.

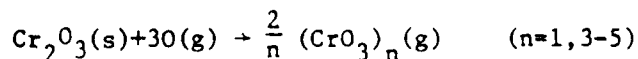
2. Convective Diffusion in Multicomponent Nonisothermal Systems

While rarely treated in engineering books on mass transport, it is shown that thermal (Soret) diffusion significantly alters convective mass transport rates and important transition temperatures in nonisothermal systems involving the transport of "heavy" species (vapors or particles). These conditions are

commonly encountered in chemical vapor deposition (CVD), partial (vapor) condensation and aerosol capture applications. Introduction of the Soret transport term is shown to produce mass transfer effects similar to those of "suction" and a chemical "sink"---indeed, this analogy provides a simple method of correlating and predicting thermal diffusion effects in the abovementioned systems. In most cases the "suction" effect is dominant, with the important group:  $\alpha_{i,w}^{0.4} (Le_{i,w})^{0.4} (T_e - T_w)/T_w$  playing the role of the dimensionless suction parameter. Here  $\alpha_{i,w}$  is the thermal diffusion factor for the transported species, shown to be a sensitive function of the molecular weight term:  $(M_i - M_{mix})/(M_i + M_{mix})$ . Even for systems in which the intrinsic thermal diffusion factors are small, we show that the apparent thermal diffusion produced by shifting (association - dissociation) equilibrium involving the transported species can be appreciable.

### 3. Oxidative-Vaporization Kinetics of Refractory Solids

Many highly refractory oxides (eg.  $Cr_2O_3(s)$ ,  $Al_2O_3(s)$ ) will vaporize more rapidly at high effective oxygen pressures than in a vacuum due to the stability of volatile oxides with the metal (or semi metal) in a higher valence state (eg.  $CrO_3(g)$  or  $AlO_2(g)$ ). We have adapted a laser optical-interference method to study such "oxidative-vaporization" phenomena, and obtained interesting preliminary kinetic data for the reaction:



in the nominal ribbon temperature range: 600 - 1000K. At the intermediate temperature (ca. 823K) of peak reaction probability we estimate that about 2.6 pct of the incident O-atoms react with chromium (sesquioxide), about 1 pct recombines, with the remaining (96.4 pct) O-atoms reflecting. We hope to extend this technique to other systems of interest (eg. boron and vanadium oxides), as well as examine analogous situations in which high effective oxygen pressures should suppress the vaporization rate (eg.  $Na_2SO_4(l)$ ,  $SiO_2(c)$  etc.

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TURBULENT MIXING AND COMBUSTION IN  
HIGH SPEED FLOWS/AFOSR-PO-78-0012

G. D. Smith and C. E. Peters

Sverdrup/ARO, Inc., AEDC Division  
Arnold Air Force Station, TN

The objective of this research is the development of reliable and physically perceptive analytical models for the turbulent mixing and heat release mechanisms in turbulent combustion systems. The approach taken in this theoretical and experimental study is to develop analytical models for the particular flow processes, then to conduct detailed experiments in order to verify and refine the models. Major emphasis is placed on the development of adequate models for (1) the turbulent transport properties for momentum, energy and mass in a variety of free and confined mixing systems, including flows with chemical reactions and recirculation, and (2) the interaction of heterogeneous turbulent mixing and finite rate chemical reaction.

During FY78, the experiments on ducted, recirculating hydrogen-air flows, both with and without chemical reaction, in a duct-to-nozzle exit diameter ratio 2.5 configuration were initiated. Wall static pressure distributions and radial profiles of total pressure, velocity and gas composition were obtained at six axial locations for a hydrogen/air mass flow ratio of 0.00345. The radial distributions of mean axial and mean radial velocity, axial and radial turbulence intensity, and the uv velocity cross correlation were obtained using a two component, Bragg-diffracted laser velocimeter. All measurements were made both with and without chemical reactions occurring. The data are being analyzed and will be reported. The test cell has been modified to permit installation of an existing laser-Raman apparatus which will be used to measure radial distributions of gas temperature and specie number density. Preliminary results indicate that the flow field for the 2.5 diameter ratio configuration is quite different from that of the diameter ratio 10 configuration previously investigated. In the larger diameter ratio case the potential core of jet fluid is dissipated before the recirculation region ends, and the flow is characterized by negligible radial concentration gradients in the downstream portion of the recirculation region. For the 2.5 diameter ratio case, the potential core of jet fluid (air) persists well downstream of the recirculation region with the recirculation region characterized by much larger radial and axial concentration gradients than were observed with the diameter ratio ten apparatus. The data also clearly demonstrate the effect of chemical reaction on the velocity field and the associated turbulent intensities.

Currently available analytical techniques and computer programs have been used to define the conditions for an interference-free supersonic wind tunnel test of the Strahle-type external-burning propulsion system.

In FY79, the experimental study on the diameter ratio 2.5, hydrogen/air system will be concluded by completing the acquisition of flow field distributions of static temperature and species number density using the laser-Raman spectroscopy apparatus. If successful, the laser-Raman measurements will be repeated in the duct-to-jet-diameter ratio ten apparatus. The data will be analyzed and a summary report containing all the experimental measurements will be prepared.

The experimental apparatus will be modified to block the annular passage and provide injection of a hydrocarbon fuel (either propane or methane) into the air stream upstream of the sudden expansion, thus providing a premixed hydrocarbon/air system. Measurements to be made in the flow field, both with and without chemical reaction, during FY79 will consist of the total pressure field, duct wall static pressure distribution, and radial profiles of the axial, radial and fluctuating velocity components obtained with a two-component, Bragg-diffracted laser velocimeter.

The results of the experimental  $H_2$ /air investigation will be compared with available analytical techniques to aid in the refinement of the analyses and the interpretation of the ducted mixing process with recirculation.

THERMODYNAMICS OF ORGANIC COMPOUNDS  
CONTRACT NO. AFOSR-ISSA-78-0009

William D. Good

Bartlesville Energy Technology Center  
Department of Energy  
Bartlesville, Oklahoma

The Thermodynamics Research Group at the Bartlesville Energy Technology Center, Department of Energy, is engaged in a continuing program of both applied and basic research on the thermodynamic properties of fuels and of organic compounds that may be useful in the synthesis and development of high-energy fuels. The research group has the skills and equipment needed for combustion calorimetry, heat capacity calorimetry, solution and adsorption calorimetry, molecular spectroscopy, pressure-volume-temperature measurements, measurement of the velocity of sound in compressed fluids, and vapor-pressure measurements. The expertise in combustion calorimetry and vapor-pressure measurement have been utilized in recent years to evaluate both fuels and compounds that have good energy characteristics per unit volume or per unit mass. This investigation has been funded by the Air Force Office of Scientific Research. Earlier research for AFOSR investigated thermodynamic properties of *elemental boron and boron compounds, elemental silicon and silicon compounds, organic nitrogen compounds, fluorocarbons, and the organic difluoroamines.*

One of the more recent endeavors has been measurement of precise values of the enthalpies of combustion of several liquid ramjet fuels. Among those fuels evaluated was *exo*-THDC, *exo*-tetrahydrodicyclopentadiene, a pure compound. Also studied were RJ-4, *exo*-tetrahydrodi(methylcyclopentadiene) and RJ-4-I, *endo*-tetrahydrodi(methylcyclopentadiene), both mixtures of isomers in which the location of the methyl groups is unknown. Measurements were made on JP-9, a blend of 10.3 weight percent methylcyclohexane, 68.4 weight percent of *exo*-THDC, and 21.2 weight percent of the hydrogenated dimers of norbornadiene. The following values were obtained for the "net" enthalpy of combustion at 298.15 K (25° C): *exo*-THDC,  $-(10081.5 \pm 2.3) \text{ cal g}^{-1}$ ; RJ-4,  $-(10153.1 \pm 2.3) \text{ cal g}^{-1}$ ; RJ-4-I,  $-(10141.7 \pm 2.2) \text{ cal g}^{-1}$ ; and JP-9,  $-(10089.5 \pm 2.4) \text{ cal g}^{-1}$ . These values refer to gaseous carbon dioxide and gaseous water as combustion products. An account of these measurements has been submitted to the Journal of American Institute of Aeronautics and Astronautics. Measurements will be performed in the near future on two similar fuels, RJ-6 and JP-10. All fuel samples were provided by G. W. Burdette, Propulsion Development Department, Naval Weapons Center, China Lake, California and James R. McCoy, Fuels

Branch, Fuels and Lubrication Division, Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio.

The studies on pure hydrocarbons involve compounds with ring-strain energies or with useful steric effects. It was found several years ago that the enthalpy of combustion of 1,8-dimethylnaphthalene is greater by 8 kcal mol<sup>-1</sup> than that of 2,6- or 2,7-dimethylnaphthalene. This finding is being pursued by the study of methyl-ethyl and methyl-isopropyl naphthalenes. Similar studies are planned on the alkyl-substituted indans that will be liquids and hence more interesting. These compounds are synthesized and purified by Professor E. J. Eisenbraun and his students at Oklahoma State University.

Similar studies under sponsorship of the Department of Energy investigate the polynuclear aromatic hydrocarbons and their hydrogenation products and also multi-ring compounds containing hetero atoms such as nitrogen.



THE EVALUATION AND COMPILATION OF  
CHEMICAL KINETIC DATA

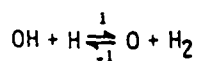
By N. Cohen and K. Westberg

The Aerospace Corporation  
El Segundo, California 90245

The Air Force currently has several programs (e.g., chemical lasers, rocket propellents) that require reliable chemical kinetic data for proper analysis and evaluation. While users of thermochemical data have a widely accepted standard reference to which to turn for much of their requirements, namely the JANAF Thermochemical Tables, the same cannot be said for kinetics. In many cases, the individuals working on Air Force problems who actually use the data are not trained kineticists themselves; they have consequently been forced to rely on a bewildering array of journals, review articles, bibliographies, tabulations, and compilations to extract what is of use to them. In many cases, there are no experimental data at all, and users must search for techniques and theories for the estimation of rate coefficients. Clearly there is a need for a set of kinetic data tables paralleling the JANAF Tables--a standardized format, compact, and reliable, that provides critical evaluations of rate coefficients; and if no experimental data are available, provides best estimates based on currently accepted theoretical and semi-empirical techniques. Such tables would also be of great use to experienced kineticists, as was argued in the recently published National Academy of Sciences report, National Needs for Critically Evaluated Physical and Chemical Data.

To this end, the Chemical Kinetics Department of the Aerospace Corporation and the National Bureau of Standards Office of Standard Reference Data received a contract for AFOSR to initiate a set of Chemical Kinetic Data Sheets. Figs. 1a and 1b give the format tentatively chosen for the reactions that are not pressure dependent. The format largely speaks for itself. Reference is made in this sheet--and in other sheets we have prepared--to previous reviews, but nonetheless all of the original literature has been critically examined and the data therein reanalyzed as required. These analyses are indicating that a sizeable percentage of the rate coefficient measurements published in the open literature cannot be used in the evaluations because of low accuracy, faulty experimental design, insufficient data to permit reanalysis or assessment of accuracy, or for other reasons.

Although the long-range goal is the evaluation of kinetic data and the compilation of data sheets for all areas of gas phase chemistry, the initial work has focused on the area of hydrogen oxidation. Other areas of interest will be decided upon after meeting with informed personnel from Air Force, NBS, and other governmental agencies. Presently it is anticipated that the work on hydrogen oxidation will be followed by evaluations in the area of hydrocarbon pyrolysis and oxidation. A second area that has received some attention already is that of hydrogen fluoride chemical lasers. The format selected is not necessarily final, and suggestions from the audience for improvement will be welcome.

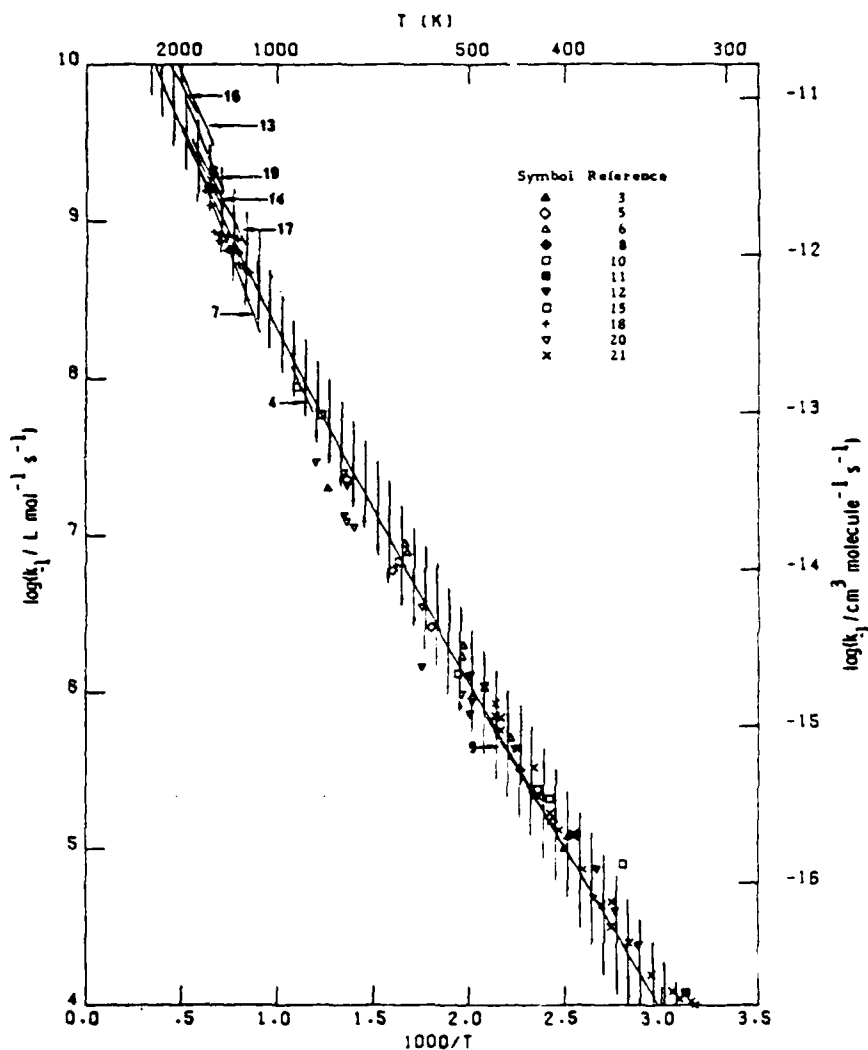


$$\Delta H_{298}^\circ = -8.54 \pm 1.3 \text{ kJ mol}^{-1} (-2.04 \text{ kcal mol}^{-1})$$

$$\Delta S_{298}^\circ = -6.72 \pm 0.06 \text{ J mol}^{-1} \text{K}^{-1} (-1.61 \text{ cal mol}^{-1} \text{K}^{-1})$$

$$K(T) = 0.445 \exp(1030/T)$$

The uncertainty in log K is  $\pm 0.2$  at 298 K, decreasing to  $\pm 0.06$  at 1000 K and  $\pm 0.02$  at 5000 K.



#### RECOMMENDED RATE COEFFICIENTS

$$k_1 = 8 \times 10^6 T \exp(-3450/T) \text{ L mol}^{-1} \text{s}^{-1}$$

$$= 1.3 \times 10^{-14} T \exp(-3450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$$

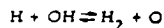
Temperature range: 400-2000 K; Uncertainty in log  $k_1$ :  $\pm 0.4$  at 300 K, decreasing to  $\pm 0.25$  at 2000 K.  $k_1$  is calculated from  $k_{-1}$  and  $K(T)$ ; its uncertainty reflects the uncertainties in both of those quantities.

$$k_{-1} = 1.8 \times 10^7 T \exp(-4480/T) \text{ L mol}^{-1} \text{s}^{-1}$$

$$= 3 \times 10^{-14} T \exp(-4480/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$$

Temperature range: 400-2000 K; Uncertainty in log  $k_{-1}$ :  $\pm 0.2$  throughout this range.

(June 1978)



#### THERMOCHEMICAL DATA

Thermochemical data for all species were taken from current JANAF Tables (June 1977). The analytic expression chosen for  $K(T)$  matches equilibrium constants calculated from these data to within 1% between 250 and 5000 K.

#### MEASUREMENTS

There have been 32 published studies of  $k_{-1}$  over the temperature range of 300 - 2000 K. There have not been any direct measurements of  $k_1$ . The reaction has been adequately reviewed by Baulch et al.<sup>1</sup> and by Dixon-Lewis and Williams.<sup>2</sup> 13 studies have been stricken from further consideration because of unreliable, obsolete, or inadequately documented data. The remaining 19 (Refs. 3-21) are plotted on the accompanying figure.

#### CALCULATIONS

A transition state theory calculation, for  $k_{-1}$  assuming a non-linear transition state for the  $\text{H} \cdots \text{H} \cdots \text{O}$  intermediate, yielded an A factor of  $10^{7.4} \text{ T}^{1.2}$  over the range of 300 - 3000 K, in good agreement with experimental data. At lower temperatures, A seems to fall below the extrapolated expression.

#### DISCUSSION

Both Refs. 1 and 2 agree on a value of  $k_{-1} = 1.8 \times 10^7 \text{ T exp}(-4480/T)$  over the temperature range of 400 - 2000 K, with an uncertainty of about  $\pm 30\%$ . This expression fits most of the data within experimental error, and we see no reason to seek an alternative. There is somewhat more uncertainty in the values of  $k$  below 400 K; some of the experimental data suggest an upward curvature in the Arrhenius plot (see accompanying figure). Although the calculations suggest the possibility of downward curvature, quantum mechanical tunneling effects could contribute to larger values of  $k_{-1}$  than transition theory predicts, and indeed Refs. 11 and 21 discuss this possibility. Because of the difficulty in assessing accurately tunneling contributions, and because of the disagreement in low temperature data, it seems desirable to reexamine  $k_{-1}$  at as low temperatures as are possible.

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Rate Constants for H, OH, and HO<sub>2</sub> Radical  
Attack on Alkanes/Grant AFOSR 77-3215

R. R. Baldwin and R. W. Walker

Department of Chemistry, Hull University,  
HULL, England.

The determination of accurate rate constants for the elementary reactions occurring in the combustion of hydrogen, carbon monoxide, alkanes, alkenes, and related compounds is of the utmost importance to a thorough understanding of the chemistry of combustion processes. It is particularly relevant at the present time because of the attention given to computer modelling, which is currently being applied to a very wide range of topics, embracing both laboratory and practical combustion units, which include atmospheric chemistry and pollution, knock in the internal combustion engine, and the combustion processes in gas turbines and rocket engines. This interest in rate constants is confirmed by the number of compilations and reviews of rate constant data which have appeared in recent years, and by the encouragement given to authors to undertake such compilations.

In the primary processes of alkane oxidation, two main types of reaction are involved. First, attack by radicals on the alkane to give alkyl radicals, and secondly, reactions of the alkyl radical in an environment of oxygen. With most alkanes, attack will occur at more than one type of C-H bond in the molecule, and it has become increasingly apparent that a satisfactory understanding of the mechanism by which the primary products are formed requires a knowledge of the relative proportions of the different radicals produced. It is only possible to obtain the proportions of each type of radical formed if the rate constants are known for radical attack specifically at each of the different C-H bond sites present for each species of attacking radical. As soon as these processes are understood, the oxidation mechanism for the primary products can be studied, so as to elucidate the complete overall mechanism of hydrocarbon oxidation.

Three main methods have been used at Hull for studying these two types of reaction involved in hydrocarbon oxidation.

- (a) Addition of alkanes and related compounds to slowly reacting mixtures of hydrogen and oxygen.
- (b) Study of the oxidation of aldehydes in the temperature range 400-550°C.
- (c) Study of the decomposition of tetramethylbutane in the presence of oxygen.

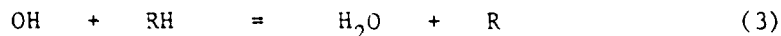
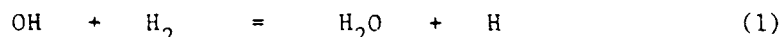
In the time available, it will only be possible to discuss the first and third of these methods.

(i) Addition of Alkanes to Slowly Reacting Mixtures of Hydrogen + Oxygen

Previous studies at Hull of the hydrogen + oxygen reaction at 500°C have enabled us to establish a detailed mechanism, and to combine our rate constants with those obtained by other workers so as to establish Arrhenius parameters for the reactions involved. Work by Dixon-Lewis has shown that the values of the rate constants in the temperature range 500-800°C are of critical importance in defining the behaviour of the hydrogen + oxygen flame. When an alkane is added in trace amounts to slowly reacting mixtures of hydrogen and oxygen in aged boric-acid-coated Pyrex vessels at 500°C and atmospheric pressure, it is removed mainly by H and OH radical attack, and thus accurate rate constants for these two processes may be obtained. The basic principle of the method may be illustrated by use of a simplified mechanism for the hydrogen + oxygen reaction, and by assuming that the alkane is solely removed by H and OH attack. In this case, the relative consumption of alkane and H<sub>2</sub> is given by equation (i).

$$\frac{d[\text{alkane}]}{d[\text{H}_2]} = \frac{k_3[\text{alkane}]}{k_1[\text{H}_2]} + \frac{Kk_4[\text{alkane}]}{k_2[\text{O}_2][\text{M}]} \quad (i)$$

where K is a constant accurately known from hydrogen + oxygen studies.



By suitable rearrangement, a linear plot may be obtained over a wide range of mixture composition, and from the gradient and intercept, values of  $k_3/k_1$  and  $k_4/k_2$  may be determined. From independent values of  $k_1$  and  $k_2$ , the rate constants  $k_3$  and  $k_4$  may be determined.

For a refined interpretation, a computer treatment allows for a number of complicating factors including:

- (a) the use of the full mechanism for the hydrogen + oxygen reaction,
- (b) the self-heating of the reaction mixture which affects the experimental pressure change used to determine the loss of hydrogen,
- (c) attack on the alkane by O atoms and HO<sub>2</sub> radicals.

Values of  $k_3/k_1$  and  $k_4/k_2$  for ethane, propane, n- and i-butane, n-pentane, neopentane, and 2,2,3,3-tetramethylbutane have been obtained at 480°C. Combination with data at lower temperatures has given Arrhenius parameters for the reactions. The results indicate that to a first approximation, rate constants

for an unknown alkane over the temperature range 25-600°C can be obtained from relationships (ii) and (iii).

$$k_3/k_1 = 0.214n_p \exp(1070/T) + 0.173n_s \exp(1820/T) + 0.273n_t \exp(2060/T) \quad (\text{ii})$$

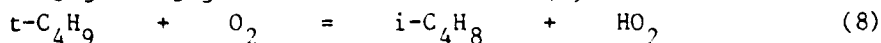
$$k_4 = 2.2 \times 10^{10} n_p \exp(-4715/T) + 4.9 \times 10^{10} n_s \exp(-4005/T) + 5.1 \times 10^{10} n_t \exp(-3030/T) \quad (\text{iii})$$

where  $n_p$ ,  $n_s$ , and  $n_t$  are the number of primary, secondary, and tertiary C-H bonds in the alkane, and  $k_4$  has units of  $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ . Use of these relationships allows the calculation of the overall rate constants and the proportions of the various species of alkyl radical formed from the alkane by H and OH attack. Recent work with 2,2,3,3-tetramethylbutane suggests that the simple additivity concept may be less secure with highly branched alkanes.

(ii) Decomposition of 2,2,3,3-tetramethylbutane in the presence of  $\text{O}_2$

This system has been developed recently to study the kinetics of  $\text{HO}_2$  radical reactions. The major problem with this radical is that most of its sources are seriously contaminated with the highly reactive OH radical which makes an accurate study of  $\text{HO}_2$  kinetics virtually impossible.

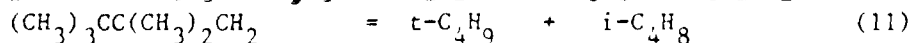
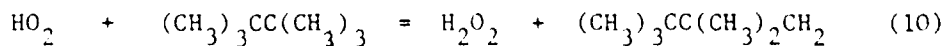
At 440°C, the decomposition of 2,2,3,3-tetramethylbutane (TMB) in KCl-coated vessels in the presence of  $\text{C}_2$  proceeds by a simple basic mechanism.



The rate of reaction is thus given by equation (iv).

$$-d[\text{TMB}]/dt = k_7[\text{TMB}] \quad (\text{iv})$$

Product analysis shows that 99% of  $\text{t-C}_4\text{H}_9$  radicals give isobutene and 1% gives isobutene oxide. Variation of the  $\text{O}_2$  pressure does not affect the rate, and at low TMB pressures and total pressures the rate equation is fully adequate. However, as the pressure of TMB is increased, the experimental value of  $k_7$  increases. Thus at 60 Torr total pressure, the value of  $k_7$  increases by about 15% over the range TMB = 0.5 to 4 Torr. The increase in the calculated rate constant is attributed to a small contribution to the consumption of TMB by the chain sequence (10) and (11).



From the increase in the experimental value of  $k_7$  with TMB pressure a value of  $k_{10}$  may be determined.

At about 440°C an added alkane such as ethane will be

removed almost entirely by  $\text{HO}_2$  attack, and from measurements of the relative rate of loss of ethane and TMB a value of  $k(\text{HO}_2 + \text{C}_2\text{H}_6) = (1.27 \pm 0.15) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at  $440^\circ\text{C}$  has been obtained. Experiments are in progress to determine the Arrhenius parameters over the temperature range  $420\text{--}520^\circ\text{C}$ . However, as the temperature is increased above  $440^\circ\text{C}$ , the system becomes more complicated, first, because the mutual reaction of  $\text{HO}_2$  radicals becomes more important due to the increased overall rate, and secondly, because hydrogen peroxide decomposes homogeneously to give highly reactive OH radicals.

Future work will extend the range of alkanes studied to determine specific rate parameters for  $\text{HO}_2$  attack at primary, secondary, and tertiary C-H bonds in alkanes, as already reported for H and OH radicals. It is also planned to use the two approaches discussed here to study the reactions of H, OH, and  $\text{HO}_2$  radicals with alkenes, which under many conditions are the major initial products in alkane combustion, and which, through their reactions, play a major part in determining the whole combustion process of the alkane.

COMBUSTION KINETICS OF SELECTED  
AROMATIC HYDROCARBONS

Richard A. Matula and Richard C. Farmer

College of Engineering  
Louisiana State University  
Baton Rouge, LA 70803

To assure adequate internal supplies of economical gas-turbine jet-fuels, the possibility of using coal and oil-shale syncrudes must be evaluated. A crucial step in this evaluation is the determination of the smoking and heating problems caused by the higher aromatic content of these newer fuels. Such concerns prompted the initiation of a research program by the AFOSR to LSU to study the high temperature pyrolysis, oxidation and carbon-formation process in selected aromatic hydrocarbon combustion systems.

The approach employed in this study will be to develop an understanding of the combustion kinetics of aromatic hydrocarbons by conducting integrated experimental and analytical studies associated with the high temperature decomposition, ignition, oxidation, and soot formation of selected aromatic hydrocarbons. Since commercial fuels are mixtures of compounds, rather than pure compounds, and since accurate kinetics models cannot be efficiently developed for mixtures, pure compounds are being studied initially. In order to understand the combustion and pyrolysis of even pure multi-atom compounds, it is advantageous to know how homologous compounds react. Toluene and benzene, the two most plentiful aromatics in both coal-syncrude distillates and unleaded gasoline, are being studied. Cyclohexane and cyclopentane were studied to show the effect of ring structure. Iso-octane and n-heptane were studied to simulate non-ring fuels with widely different ignition characteristics. Investigations of mixtures and of high-boiling-point, multiple-ring aromatics have not yet been considered.

Progress is being made in all aspects of this study. The single-pulse shock-tube provides pressure data from which ignition delays may be determined and samples of quenched reaction products may be obtained. The quenching freezes the pyrolysis and oxidation at intermediate degrees of completeness so that stable products present at that time may be determined. These samples may be analyzed with gas chromatography. The conventional shock-tube provides optical data in both the IR and UV to determine radical and stable species concentrations, as well as laser-beam extinction measurements for soot formation studies. The analytical contribution to this study will be made with existing computer programs. This analysis requires the specification of certain thermodynamic and kinetic data to specialize case-studies to the particular aromatic systems of interest. The status of each phase of this study is described in sequel.

Ignition delay times for several hydrocarbon fuels were



measured to establish relative ease of combustion initiation. All six of the previously mentioned fuels were studied. The comparisons were made with stoichiometric mixtures of fuel and oxygen, which were highly diluted with argon. The initial concentrations of the fuels were equal in carbon atom concentrations, i.e., the concentration in molar units of toluene was 6/7 of that of benzene while that of cyclopentane was 6/5 of benzene. Pressures behind the reflected shock were approximately 4 (atm). A plot of the common logarithm of the ignition delay time versus the calculated frozen shock temperature behind the reflected shock wave is presented. Experimental points and least-square fits were plotted for each fuel except toluene. Initial compositions as well as apparent activation energies in (kcal/mol) resulting from the curve fit are also presented.

Since pyrolysis and oxidation studies of benzene have been previously published; toluene was chosen for a more detailed ignition delay study. Five toluene/oxygen/argon mixtures were studied in seven groups of experiments to establish the empirical equation stated below.

$$\tau(\mu\text{sec}) = 8.94 \times 10^{-15} (\exp(56.5 + 3.6/RT)) [O_2]^{-1.76 \pm 0.18} [Ar]^{0.64 \pm 0.17}$$

where  $\tau$  = ignition delay time,  $\mu\text{sec}$   
 $R$  = universal gas constant, kcal/mol $\cdot$ K  
 $T$  = temperature, K  
 $[ ]$  = concentration, moles/cc

An exponent for toluene was found to be zero within the statistical accuracy of this determination. The logarithm of the constant  $8.94 \times 10^{-15}$  is determined to be known to  $\pm 10\%$  (within 95% confidence limits). This means that this equation for ignition delay time should not be extrapolated to concentration conditions far removed from the experimental conditions for which it was determined.

Incipient soot formation during the oxidation of toluene has been measured. The upper limit temperature and lower limit temperature for incipient soot formation on shock heated toluene/oxygen/argon mixtures have been measured for atomic carbon to oxygen ratios from 1 to 2. Typical partial pressures of toluene behind the reflected shock waves were 11 torr. Extinction of light from a He-Ne laser at 6328 ( $\text{\AA}$ ) was used to detect soot.

During the course of these experiments, an induction period ranging from approximately 20 to 2600 ( $\mu\text{sec}$ ) was observed before the absorption signal occurred. This period has been defined as the soot formation delay time,  $\tau_{\text{soot}}$ . It is interpreted as the time required for the fragmentation and condensation process to form soot. Therefore, it is postulated that the measurement and correlation of soot delay time can be a useful tool in studying the combustion kinetics, of soot formation. The following empirical formula for correlating delay times is postulated:

$$\tau_{\text{soot}} = A \exp(+E/RT) (\text{fuel})^a (O_2)^b (Ar)^c$$

Sufficient data are not presently available to determine the power dependencies of  $\tau_{\text{soot}}$  on the concentration of fuel, oxidizer and inert gas. A least-squares correlation of preliminary data yields an estimate of the parameters A, a, b, c, and E:

$$A = 3\text{E-}04 \qquad a = b = c = 0$$

$$E = 46.3 \pm 5.4 \quad (\text{kcal/mol})$$

The units on A are such that  $\tau_{\text{soot}}$  is in ( $\mu\text{sec}$ ). The value of A is not well defined by these preliminary experiments.

Aromatic pyrolysis and combustion are being analyzed by two approaches: (1) empirical correlations and comparisons are being established to expedite the direct use of experimental data and the formulation of global-rate equations; and (2) the development of detailed mechanistic models for aromatic combustion has been initiated. Since the fuel molecules of interest are large, their reactions are very complex and they produce many intermediate compounds and radicals. Toluene has been chosen as a typical aromatic fuel for which a detailed kinetics model will be developed.

Fuels Combustion Research  
(Contract F49620-78-C-0004)

F.L. Dryer and I. Glassman

Princeton University  
Princeton, New Jersey 08540

Interest in chemically related combustion problems has led to an integrated fuels research program under AFOSR support. If improvement in performance and general emission characteristics is to be achieved, a better understanding of the coupled fluid mechanical and chemical kinetic processes occurring in propulsive systems must be gained. Research emphasis is on the pyrolysis and oxidation of aliphatic and aromatic hydrocarbons, soot formation/destruction and carbon oxidation.

Detailed results on the pyrolysis and rich oxidation of ethene have been obtained. In addition pyrolysis studies of propane have been undertaken. Overall reaction rate expressions have been derived for each and a detailed kinetic model has also been assembled for the propane pyrolysis results.

The kinetics of the ethene pyrolysis and oxidation were studied in a turbulent flow reactor at atmospheric pressure. Pyrolysis experiments with  $C_2H_4$  highly diluted in nitrogen (0.3 to 1.0%  $C_2H_4$ ) show  $C_2H_2$  and  $H_2$  as the major reaction products together with small amounts of butadiene and traces of  $CH_4$  and  $C_2H_6$ . The study covers the temperature range from 1160 to 1260K and results are compared with previous investigations. An overall mechanism is proposed which is consistent with results of both previous studies and the current work.

The analysis of ethylene oxidation experiments ranging from 950 to 1110K exhibits a broad spectra of intermediate and final oxidation products. The variation of the oxygen concentration over an extended range corresponds to equivalence ratios from 11 to 1. In this fuel rich regime the  $C_2H_4$  exhibits a fuel order dependence of 0.8 and is strongly dependent on the oxidizer concentration. From a correlation of the rate data the following expression has been deduced:

$$-\frac{d(C_2H_4)}{dt} = 10^{20.3} \exp(-50,300 + 3000/RT) (C_2H_4)^{+0.8} (O_2)^{+1.5}$$

This rate expression has to be understood as an empirical description of the overall reaction rate dependence on temperature, oxygen, and fuel concentration. The activation energy as well as the pre-exponential factor do not necessarily represent arrhenius parameters as known from elementary reactions.

A study of propane pyrolysis has been undertaken to elucidate important fuel radical reactions occurring in the pyrolysis process. Although the general features of the pyrolysis mechanism are agreed upon, detailed understanding is still lacking.

A series of pyrolysis experiments for the temperature range of 1120 to 1240K have been conducted over a propane concentration range of  $1.2 \times 10^{-8}$  to  $1.2 \times 10^{-7}$  moles/cc. Consistent with previous investigators the major products observed are ethene, propene, methane and hydrogen with smaller amounts of ethane, acetylene and butadiene. Analysis of the pyrolysis results have proceeded from two independent approaches: an overall rate approach and a detailed kinetic model approach.

The overall rate has been derived assuming first order fuel dependence and results in the following expression:

$$-\frac{d(C_3H_8)}{dt} = 10^{12.5} \exp(-58650/RT) S^{-1}$$

Comparisons of these results with other workers show good agreement over a wide range of temperatures.

In order to provide a more detailed representation of the pyrolysis mechanism a twenty-one reaction step mechanism has been assembled to represent the observed results. Reactions involving initiation, hydrogen atoms or methyl radical obstruction, as well as iso and normal propyl radical reaction paths have been shown to be important in accounting for the results.

Data on the high temperature oxidation of toluene have been obtained on the Princeton flow reactor and the oxidative rate characteristics have been observed to differ markedly from the aliphatics. Product profiles show the copious production (in comparison to alkane systems) of acetylene well into the lean region of the reaction. This would be expected for a fuel with high sooting tendency.

In addition, experiments dealing specifically with the formation and destruction of soot in various hydrocarbon diffusion flames have been undertaken. A comprehensive review and analysis of practical results of inhibitors suggests that formation of hydroxyl radicals is a key to soot prevention. However initial studies of effects of water addition to soot precursor formation have been inconclusive. Overall experiments utilizing apparatus developed during the current program have pursued the measurement of sooting height as an indication of sooting tendency. Sooting height characteristics of several fuels and fuel mixtures have been made including a mixture of toluene and heptane.

A second approach involving premixing of fuel and soot

inhibitors in a diffusion flame burner has been developed and initial experiments are underway.

ABSOLUTE RATE CONSTANTS FOR REACTIONS  
OF RADICALS IMPORTANT IN COMBUSTION PROCESSESD. F. McMillen and D. M. Golden  
SRI International  
Menlo Park, CA 94025

A quantitative understanding of the chemical kinetics of combustion requires a knowledge of the rates of formation and destruction of the pertinent radical species. This knowledge, in turn, is critically dependent on the capability for reliable extrapolation of rate constants from the lower temperature ranges in which they are usually measured to temperatures of interest in combustion. This can be difficult not only because the determination of Arrhenius parameters with sufficient accuracy for reliable temperature extrapolation is itself difficult, but because temperature ranges of interest may substantially exceed that over which a simple Arrhenius expression can be expected to successfully correlate rate data. Furthermore, at the high temperatures of interest in combustion, chemical reaction rates can easily be sufficiently rapid that energy transfer to the molecule(s) undergoing reaction can be rate-limiting, and the reaction rate "constants" will be in the pressure dependent, or fall-off, region. Extrapolation of rate data under these conditions is possible within the framework of transition state theory and statistical mechanical theory (RRKM Theory and recently developed simplifications<sup>1</sup>), but this requires application of the proper transition state models, and a knowledge of the limitations of transition state theory.

We briefly describe here a number of results obtained under the sponsorship of AFOSR and several other agencies which are a part of our effort to achieve the necessary systematic understanding of the temperature, pressure, and structure dependence of the various reaction rates.

The data include absolute rates for bond scission, radical recombination, and hydrogen-transfer reactions, as well as heats of formation for the respective radicals, all determined by the technique of very low-pressure pyrolysis. The radicals chosen for study were allyl, benzyl, 1-methylnaphthyl, and t-butyl radicals. These radicals are all important in the combustion of aliphatic and aromatic substrates and/or are species whose reported thermochemical parameters have recently been questioned.<sup>2</sup> In addition, whereas there is now little question that the recombination of saturated hydrocarbon radicals proceeds with little (often negative) or no activation energy,<sup>3</sup> the gas-phase recombination of resonance-stabilized radicals

Using diallyl oxalate, 3,3'-azo-1-propene, diallyl, dibenzyl, benzylvinyl ether, ethyl benzene, 1-ethylnaphthalene, and neopentane as sources of allyl, benzyl, 1-naphthylmethyl, and t-butyl radicals, study of the reactions listed in Table I provided the indicated thermochemical and kinetic parameters.

Ref	Reaction	Temp. Range	Log A <sup>a</sup>	E <sup>b</sup>	Radical Thermochemistry	
					$\Delta H_{f,298}^\circ$ <sup>b</sup>	RRS <sup>b</sup>
6	$2 \text{ } \text{Cyclohexene} \xrightleftharpoons[k_d]{k_r} \text{Cyclohexadiene} + \text{Cyclohexadiene}$	635 844-923 980-1080	10.06 ± 0.07 10.39 ± 0.15 14.3 ± 0.15	— — 54.5 ± 1.0	38.3 ± 1.5	12.5 ± 2.0
7	$\text{Cyclohexene} + \text{HI} \xrightarrow{k_p} \text{Cyclohexane} + \text{I}^\cdot$	900-1000 635- 770	9.73 ± 0.21 9.56 ± 0.35	4.0 ± 1.0 3.0 ± 1.0	39.1 ± 1.5	11.7 ± 1.5
7	$\text{SCCH}_3^\cdot + \text{DI} \xrightarrow{k_p} \text{SCCH}_3\text{-D} + \text{I}^\cdot$	811-1126	9.93 ± 0.22	4.0 ± 1.0	46.6 ± 1.5	11.3 ± 2.0
8	$\text{SCCH}_2\text{CH}_3 \xrightarrow{k_d} \text{SCCH}_3^\cdot + \text{CH}_3^\cdot$	970-1180	15.4 ± 0.3	(73.4 ± 1.0) <sup>d</sup>	(45.0 ± 1.0)	(12.9 ± 1.5)
8	$\text{SCCH}_2\text{CH}_3 \xrightleftharpoons[k_r]{k_d} \text{SCCH}_3^\cdot + \text{CH}_3^\cdot$	970-1143 1100 (k <sub>r</sub> )	15.2 ± 0.3 9.4	66.7 ± 1.8 —	57.0 ± 1.8	16.3 ± 1.1
9	$(\text{CH}_3)_3\text{C-CH}_3 \xrightarrow{k_d} (\text{CH}_3)_3\text{C}^\cdot + \text{CH}_3^\cdot$	1000-1260	17.3 ± 0.8	(80.4 ± 1.5)	8.4 ± 2.0	—
20	$(\text{CH}_3)_3\text{C}^\cdot + \text{DI} \xrightarrow{k_p} (\text{CH}_3)_3\text{C-D} + \text{I}^\cdot$	600-700	—	—	8.4 ± 1.0	—

<sup>d</sup> Values in parenthesis represent literature values.

The principal generalizations to be made from these results are:

- (1) The recombination of allylic radicals is essentially as fast as that of saturated radicals, in spite of the fact that saturated radicals have no delocalization energy to be lost on recombination.
- (2) Similarly, hydrogen abstractions by allylic and benzylic radicals proceed at rates consistent with small positive activation energies. For allyl, benzyl, and t-butyl radicals, the measured values in the range 635 to 1000 K are consistent with 1.5 - 2.5 kcal/mole at 500 K.
- (3) Neither the hydrogen abstraction rate parameters nor the neopentane pyrolysis are easily reconciled with recently published values<sup>2</sup> for the heat of formation of t-butyl radical of  $10.5 \pm 1.0$  and  $12.6 \pm 1.0$  kcal/mole, but require, instead, values of  $8.4 \pm 1$  and  $8.4 \pm 1.5$  kcal/mole, respectively.<sup>9,10</sup>
- (4) The resonance stabilization energy of the 1-naphthylmethyl radical is  $3.6 \pm 1.1$  kcal/mole greater than that for benzyl radical, in good agreement with a recently developed estimation method for benzylic radical resonance stabilization energy.<sup>11</sup>
- (5) The recombination rate constant for the methyl--1-naphthylmethyl--radical recombination appears to be lower than would be expected were its behavior analogous to that observed for allyl radical. This disagreement has not been either resolved or fully confirmed as of the writing of this abstract.

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## AIRBREATHING PROPULSION COMBUSTION TECHNOLOGY IN AFAPL

Ken Hopkins  
Components Branch  
Turbine Engine Division

Within the Aero Propulsion Laboratory, there are two groups which deal with turbine engine combustion technology: the Combustion Technology Area, under the Turbine Components Branch of the Turbine Engine Division; and the Fuels Technology Area, under the Fuels and Lubrications Division. The Combustion Technology group deals with hardware influences on the combustion system while the Fuels Technology group deals with the influence of fuel composition and characteristics on combustion processes. The combustion technology program that will be highlighted during this presentation is that of the Combustion Technology group. The basic combustion technology needs of both groups, however, are nearly the same.

The Combustion Technology Group of the Air Force Aero Propulsion Laboratory is responsible for development of new technology and hardware systems which meet the gas turbine combustion needs of the Air Force. Principal research and development efforts encompass the main combustor and augmentor systems plus mathematical modeling activities related to both.

The areas of technology required to meet the Air Force combustion systems technology needs cover a broad spectrum of scientific disciplines. Combustion, thermodynamics, gas dynamics, heat transfer, structures and materials are major disciplines required to carry out the Air Force's program of exploratory and advanced development. These technical disciplines are directed at major development facets such as concept definition, modeling, stability and emissions/efficiency to produce advanced technology combustion systems which can be engine demonstrated.

Current programs include Combustor Design Optimization, a mathematical modeling effort, and the Folded-Pilot Swirl Combustor Development Program. Additionally, a program on Augmentor Combustion Stability was recently completed.

The Combustor Design Optimization program is an effort at Purdue University under the Laboratory's Senior Investigator program to analyze combustion/combustor flow models. This program is scoped to define areas of weakness within the numerical models, provide refinements as necessary and to design experiments necessary to provide data to resolve deficiencies and validate model predictions.

The Folded-Pilot Swirl combustor is a technological advancement of the Pratt & Whitney Radial-Pilot Swirl Combustor. These swirl combustors are applicable to high thru flow engines having inherently high Mach number compressor discharge flow fields. The new folded-pilot concept utilizes the same main combustor but the pilot is

folded over the main combustor to provide a significant length reduction. Also, the staged fuel injection system is eliminated by providing dual-orifice injectors in the pilot thus significantly reducing the complexity of the combustor fuel distribution system. This cost-shared program is currently entering the component test phase. Development of the pilot combustor and fuel nozzles is complete.

Augmentor low frequency combustion instability (rumble) has been investigated under three contracts which have recently been completed. Rumble mechanisms and causes have been studied, and a computer model has been developed to analyze the rumble potential of designs at various operating conditions. The model was tested as part of the joint Air Force/NASA Full Scale Engine Research program at Lewis Research Center.

A new program to be started this fall is the Advanced Material Segmented Combustor Program. The objective of this effort is to demonstrate the feasibility of employing nonmetallic/ceramic segments in a combustor liner. The program will investigate segment designs which will preclude the formation of high thermal stresses causing failure in designs employing large pieces or monolithic structures. Subsequent demonstration testing will define the limiting temperature of the non-metals being investigated.

Another new program to start this year is the Variable Geometry Combustor Development Program. Although variable geometry features translate to increased mechanical complexity, the benefits resulting from controlled and/or optimized airflow and fuel flow distribution at all power settings will provide improvements in altitude relight, ground starting, combustion stability and exhaust emissions in high temperature rise combustors. This contracted effort will commence with a state-of-the-art review of current technology followed by construction and test of several candidate combustor designs. The most promising configuration will then be developed into a full-scale burner to be tested and later incorporated into an Advanced Demonstrator Engine program. This program is jointly sponsored by the Air Force Aero Propulsion Laboratory, the Air Force Civil and Environmental Engineering Development Office and the Naval Air Propulsion Center.

A new in-house turbopropulsion Combustion Technology Assessment program began in March. In this program the military engine contractors are working with the Laboratory to provide a technical assessment of combustion system design and performance identifying technology needs for use in formulating the FY80-85 Long Range Technology Plan.

The current and coming programs point out the Air Force's near-term interests in advanced aerodynamics and high durability combustor designs. Improvements in all of the basic technology disciplines mentioned above are needed if the Air Force is to reach its goals. Specific basic research needs of the Combustion Technology group include reaction kinetics, turbulence/mixing, heat transfer (convection/radiation), combustion instability, and diffusion. Basic research in areas such as stress profiles, material properties, is of interest, but in a

less direct way. Advances in areas such as material properties must be in a highly refined state, such as a new material which has been through manufacturing technology development. To the Combustion Technology group, the most important and useful of basic research is advancements in understanding of combustion, aerodynamics (turbulence, diffusion, droplet/two-phase flow, etc.) and heat transfer phenomena. Such advancements can be directly applied to developing new combustor designs without secondary development of the new technology.

Fundamental Modelling of Kinetics, Mixing and  
Evaporation in Combustors (Grant 74-2682)

J. Swithenbank

Sheffield University  
Sheffield, England

Practically all the propulsion systems currently employed by the USAF burn fuel, in the form of liquid hydrocarbon, in combustors. The design of the combustors for optimum efficiency, often over wide operating conditions, presents many severe unsolved problems. Currently available design methods are based on empirical correlations and result in slow and expensive development procedures. To date, it has not proved possible to devise a design method based on fundamental considerations due to the complexity of the system which involves interaction between droplet evaporation, turbulent mixing and chemical kinetics.

However, 3-dimensional 2-phase mathematical models, which predict the local values of the dependent variables have now been developed and tested against experiment. This paper presents profiles of hydrodynamic and thermodynamic patterns in a gas turbine combustor obtained by means of a well-established numerical prediction algorithm. The prevailing distribution of the dependent variables in the steady, turbulent, chemically reacting environment considered, is achieved by solving the governing differential transport equations. The pertinent features of turbulence are simulated via models incorporating the distribution of kinetic energy of turbulence and its dissipation rate. Spray combustion is computed from the droplet trajectories and evaporation to yield concentrations of the discrete size groups of droplets. Chemical reaction is assumed to proceed in two distinct steps, thereby enabling local concentrations of CO, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O and fuel to be evaluated. Predictions have also been obtained for the case of a diffusion flame with both premixed, pre-vaporized fuel and spray fuel. It is shown that a two dimensional model can be used in the immediate vicinity of the fuel nozzle.

Complementary to the above algorithm, a procedure for predicting pollutant formation has been formulated in terms of inter-connected stirred and plug flow reactors to handle realistic chemical kinetics, unmixedness, and evaporation. This presently considers 13 species undergoing 18 reactions to model the combustion of kerosene. Concentrations of minor constituents of combustion are predicted in order to study in detail the pollutant formation mechanisms.

Attention is drawn to some of the current difficulties in these modelling procedures, nevertheless, in spite of the inherent physical and mathematical assumptions involved, predictions from both sections of study reveal remarkably good agreement with experiments.

Future work involves: 1) the modelling of dump combustors; 2) the development of techniques to speed-up and hence reduce the cost of the computation procedures, 3) extensive experimental verification of the models to ensure their reliability over a wide range of operating conditions, and 4) the development of a method of evaluating the appropriate stirred reactor network by correlating pseudo-random input and response on a water model of the combustor.

MECHANISMS OF RADIATION AUGMENTED  
IGNITION AND COMBUSTION  
Contact No F49620-77-C-0085

Dr. Anthony E. Cerkanowicz

Exxon Research and Engineering Company  
Government Research Laboratories  
P.O. Box 8, Linden, New Jersey 07036

Aircraft operating limitations due to combustion and associated phenomena such as flammability, flame propagation, ignition and stable combustion are becoming increasingly important in advanced military aircraft. These limitations originate in part from system design factors rather than inherent combustion phenomena. One of the techniques which is being explored to circumvent these limitations is the use of ultra-violet radiant energy. Other augmentation techniques which will be assessed include massive heat exchange, centrifugal force, catalysis, plasma torch exposure and improved spark discharge. The impact of these novel augmentation techniques on combustor operating characteristics will be delineated in the proposed effort. Demonstration of feasibility and the development of realistic design criteria for the most effective augmentation approaches will be the major goals of the study.

There are potential advantages when using a combustion augmentation technique because of the basic difference by which a stable combustion wave is created compared to the thermal effect generated by spark igniters. The initial reactions created by augmentation, such as irradiating a combustible mixture with ultraviolet light, are not governed by the usual thermal reaction kinetic parameters, and thus it is possible to initiate self-sustaining reactions at pressure and temperature conditions other than those required with a thermal spark system. For example, the relight capability of military turbine engines at high altitudes and low combustor inlet pressures and temperatures should be restricted only by the blow-out limit of the combustor configuration. Further, the ultraviolet light irradiation method, does not have pressure limit where the igniter becomes inoperative as a consequence of the radiation source electrodes being protected from the combustor environment pressure. Therefore, a photochemical ignition system should have wider ignition capabilities in terms of the combustor inlet air parameters of pressure, temperature, and velocity.

New aircraft engines manufactured after 1979 will have to meet stringent emission standards. Combustors designed to meet these standards could have difficulty achieving ignition and relight capability with the standard spark igniter because of the igniter sensitivity to local fuel-air ratios. The augmentation techniques proposed are considerably less sensitive to local fuel-air ratio at light-off, and therefore may provide a practical method of maintaining more acceptable ignition and relight capabilities with the emission-controlled engines of the 1980's.

Four light source systems have been selected for use in the experimental program as listed below:

<u>Source</u>	<u>Description</u>	<u>Wavelength Range (nm)</u>
ILC	Pulsed, point source (VUV)	140-250
ORC	Continuous, 1kW, focused or parallel beam (UV)	200-400
EIMAC	Continuous, 500W, focused beam (VUV/UV)	155-400
EXXON	Pulsed, xenon dimer laser (VUV)	162-182

The first three sources are high pressure xenon-plasma, short-arc systems. The pulsed, vacuum ultraviolet (VUV), point source design is based on improved versions of the previous designs utilized for photochemical ignition. Fabrication of these sources is currently in progress. The continuous radiant sources were selected from product lines after a thorough screening process. The xenon dimer laser is an electron beam driven system that exists as part of the Exxon Research Center facilities. A vacuum ultraviolet spectrographic facility has been set up to characterize light source spectral output. Light source intensity and pulse shape measurements are being undertaken as a function of wavelength, energy/power input, distance from light source window, and window area.

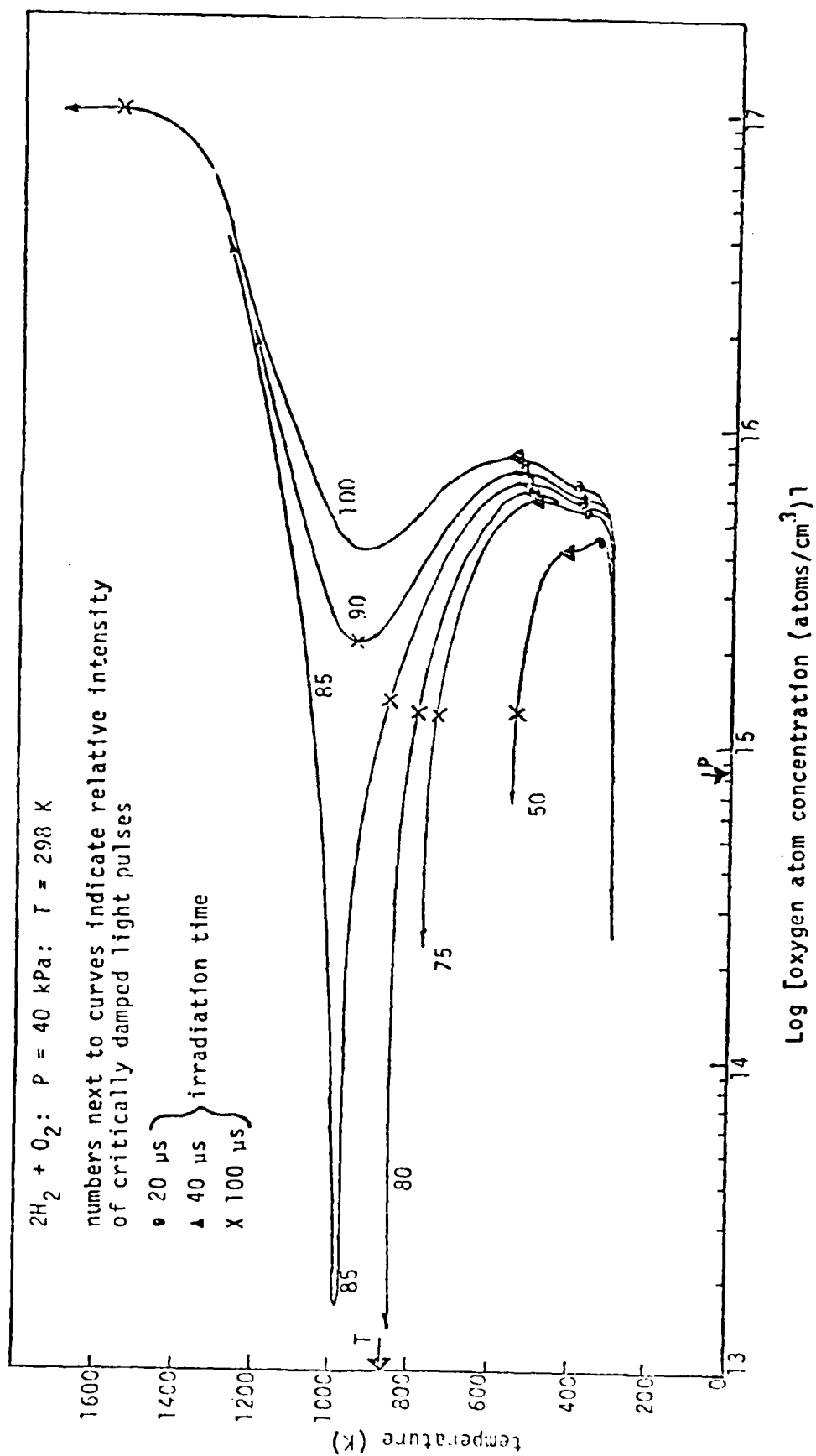
A stationary reactant mixture combustion cell has been fabricated to characterize light source-reactant mixture interaction. Combustion initiation can be studied using either VUV light sources, in situ spark discharge or a combination of both. A photodetector array is utilized to record flame propagation speeds following the ignition process. An adjustable length cell will be used between the reactant chamber window and light source to investigate the influence of a fuel-free air layer on ignition requirements. The influence of UV sources on ignition and subsequent flame propagation will be studied using the spark discharge as the primary reaction initiator.

A complimentary effort involves the development of analytical capability for modeling photochemical initiation and enhancement of combustion. Physical and chemical events considered in the model include: radiant absorption by reactant and combustion-intermediate species according to the Beer-Lambert law, chemical reactions including photodissociation and excited state kinetics. Diffusion of species along the direction of the light beam, and wall recombination at the light source window will be included in subsequent versions of the model. Wavelength dependent absorption cross sections for  $O_2$ ,  $O_3$ ,  $H_2O$ ,  $HO_2$  and  $H_2O_2$  are utilized. Light source characteristics considered are window transmission (wavelength dependent), beam spreading angle, pulse time, and intensity (wavelength, time, input energy dependent). The current model is specifically limited to  $H_2$ - $O_2$ - $N_2$  systems. In computations where the reactant temperature is allowed to increase, each element of the gas is treated as an adiabatic system. No convective or conductive heat transport is allowed.



The following Figure illustrates model predictions for the irradiation of a 298 K, 40 kPa, hydrogen-oxygen mixture. Each curve represents a photochemical path (time implicit) in the phase plane for a given radiant intensity. The radiant pulse was assumed to be a critically damped discharge with a time to peak intensity of 20  $\mu$ s. For low radiant intensities (50, 75, 80) the radiant pulse generates oxygen atoms and some temperature rise, but the final tendency of the mixture is to return to the initial conditions that existed before irradiation. At higher radiant intensities (85, 90, 100), the irradiated mixture has entered the unstable zone and the tendency to return to the initial conditions is overcome. All of these high intensity conditions eventually result in rapid burning (combustion). Care must, however, be exercised in using these results since the current program does not include heat loss and the kinetic rates used are valid only over a temperature range of 298 to 1500 K.

Although the results indicated are preliminary, qualitatively the predicted behavior compares very favorably with previous description based on general phase plane analysis. Quantitatively, the oxygen atom concentration achieved during the initiation phase (time less than about 100  $\mu$ s) is about 80-85 times greater than estimated previously based on experimental measurements. Detailed results on light source characteristics, and exploration of kinetic and absorption data in the current program should provide for rectification of this difference.



Phase plane paths for a stoichiometric hydrogen-oxygen mixture irradiated  
 with various VUV pulsed light intensities.

## PHOTOCHEMICAL COMBUSTION ENHANCEMENT

Raymond C. DesMarais, Jr.  
Ole A. Sandven, ScD  
James R. Bolten, PhD

RIGS Corporation  
51 Middlesex Street  
North Chelmsford, Mass. 01863

This report describes the introduction of sensitizers to fuels, and the creation of long-lived radicals by irradiation of this fuel mixture prior to ignition of the internal combustion engine.

While experiments have been performed on continuous fuel flow combustion in steam boilers in addition to automotive engine testing, we have not applied our technology to the gas turbine.

Because of reports by other workers in this field of interest, i.e., Norrish, Cerkanowicz, Lee, et al., irradiation of an appropriate sensitizer immediately prior to the combustion zone of a gas turbine engine seems worthy of serious examination. \*

We have focused upon the addition of UV-absorbing sensitizers to fuels in reserve tanks, or enroute to the combustion zone, and then irradiating the mixture to produce oxygen and/or hydrocarbon free radicals just prior to the initiation of combustion.

Our objective is to provide pre-combustion enhancement of fossil fuels. We think the early introduction of free radicals enables the pre-ignition reactions with hydrogen atoms in the fuel. If this is true, it may provide the rationale for various engine re-adjustments now available, i.e., the timing, and leaner air/fuel mix ratios.

While our testing has not been entirely rigorous, we have compared results of various sensitizers and levels of UV radiation. (See attached Table II. from our test report.)

This table is not completely informative because of the proprietary nature of the compounds and UV intensity levels. Our patent attorney informs us that the U. S. Patent Office examiner has indicated that the claims in our initial application are to be allowed shortly.

Our second application now in process encompasses our work on continuous fuel flow to steam boilers.

Our future work will include three basic efforts: 1) to complete tests in industrial power generation and steam-making combustion

enhancement via photochemistry, 2) to refine our approach to lower pollution levels and increased fuel economy, or better performance, in the internal combustion field, and 3) to explore a gas turbine investigation with an interested party.

(Attachments No. III, Cases A and B are electron spin charts illustrating the presence of free radicals when the effluent from our reactive intermediate generator was absorbed by Phenyl N-tertiary-Butylnitronone.)

*\* This method is the subject of one of our patent applications in the field of continuous fuel flow combustion enhancement.*

## II. ROAD TESTS: MPG RESULTS

<u>TEST CONDITIONS</u>				<u>MPG</u>	<u>MPG</u>	<u>SPEED</u>	<u>COMMENTS</u>
<i>(FUEL ADDITIVES)</i>				<i>AVERAGE</i>	<i>GROSS</i>	<i>MPH</i>	
Baseline I.				N.A.	24.35	52-54	
Baseline II.				N.A.	26.60	52-54	
Baseline III.				27.29	27.09	53.93	
				-	-	-	
5 ml	/Gal.	L.I.		28.16	27.99	51.98	
"	"	"	M.I.	N.A.	29.43	54.90	--- Interrupted test
"	"	"	H.I.	28.90	27.86	51.87	
10 ml	/Gal.	L.I.		28.45	27.73	N.A.	
"	"	"	M.I.	29.41	28.87	54.30	
"	"	"	H.I.	28.80	28.48	53.86	
20 ml	/Gal.	L.I.		28.31	28.07	54.82	
"	"	"	M.I.	27.70	27.51	53.96	--- Windy
"	"	"	H.I.	29.44	29.07	53.86	
5 ml	/Gal.	L.I.		N.A.	N.A.	N.A.	
"	"	"	M.I.	28.91	28.41	53.93	
"	"	"	H.I.	29.93	29.27	54.05	
20 ml	/Gal.	L.I.		29.35	28.49	52.92	
"	"	"	M.I.	29.13	29.26	53.88	
"	"	"	H.I.	30.78	29.22	53.11	
5 ml	/Gal.	L.I.		28.59	28.40	52.96	
"	"	"	M.I.	29.53	28.49	53.34	
"	"	"	H.I.	29.65	28.33	52.91	
10 ml	/Gal.	L.I.		29.15	28.81	52.92	
"	"	"	M.I.	29.47	29.08	52.69	
"	"	"	H.I.	N.A.	N.A.	N.A.	
20 ml	/Gal.	L.I.		29.60	28.83	53.40	
"	"	"	M.I.	30.48	30.04	54.15	--- Windy
"	"	"	H.I.	30.03	29.02	53.36	

# III. ELECTRON SPIN CHARTS OF "EXTERNAL" UNIT OUTPUT

EPA Recordings . . .

VARIAN spin Resonance

Scan Range 500 G Time Constant 1.0 sec Modulation Amplitude 1.6 G Receiver Gain  $\times 10^3$  Microwave Power 10 mW Operator RSH Date 3/17/77

Field Set 3000 G Scan Time 4 hrs min Modulation Frequency Hz Temperature RT °C Microwave Frequency 9.100 GHz

CASE A: Phenyl N-tertiary Butylnitron

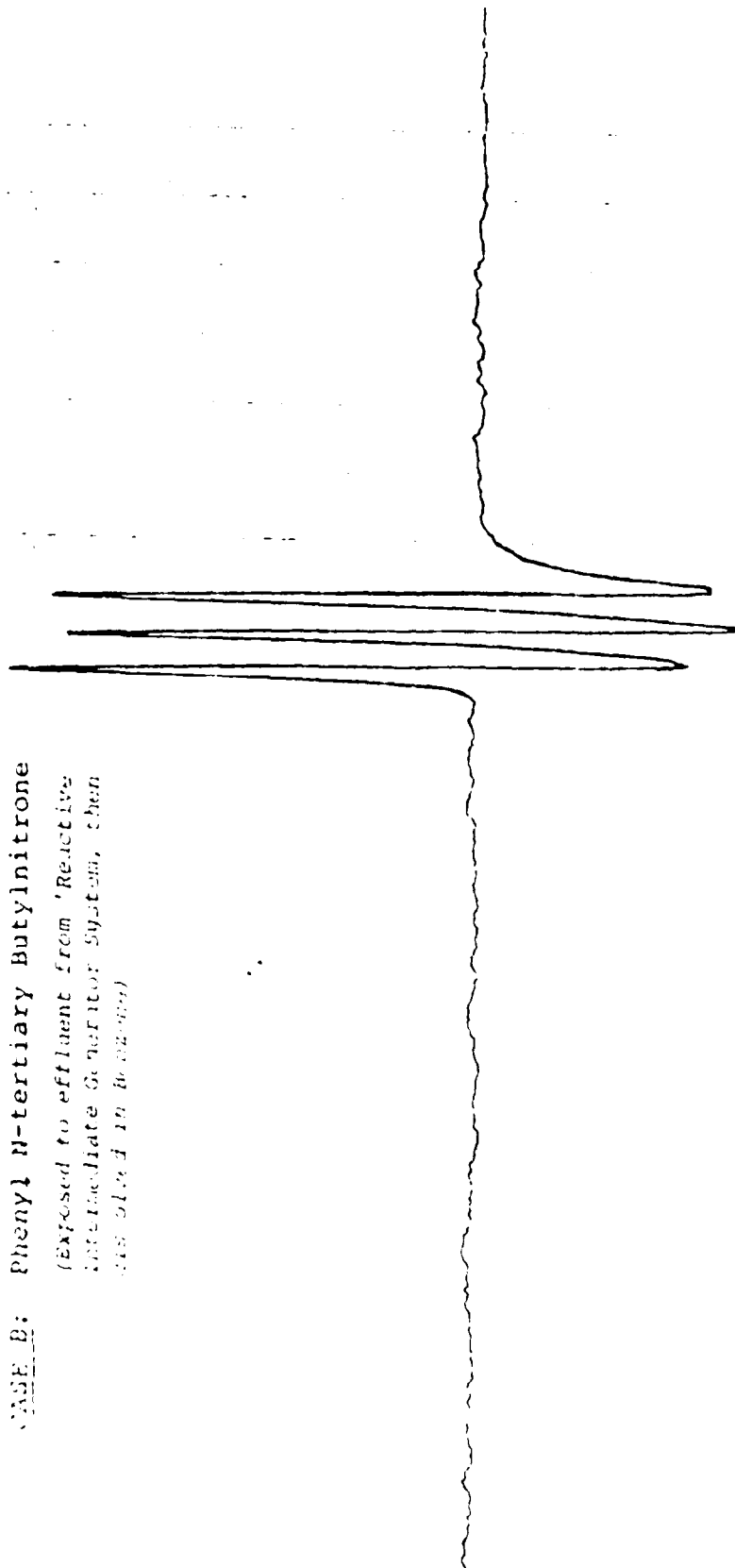
(Trapping compound dissolved in Benzene)



Scan Range 500 G Time Constant 10 sec Modulation Amplitude 1.6 G Receiver Gain 5 x 10<sup>3</sup> Microwave Power 10 mW  
 Field Set 3225 G Scan Time 4 hrs Temperature RT °C Microwave Frequency 9.100 GHz Date 3/17/77 Operator RSH

CASE B: Phenyl N-tertiary Butylnitrone

(Exposed to effluent from 'Reactive  
 Intermediate Generator System, then  
 was placed in the cell)



Air Force Supported Research Program and Needs  
Associated with Gas Turbine Engine Emissions and Other  
Combustion Related Problems

Capt Harvey J. Clewell  
Capt Joseph A. Martone

Environmental Sciences Division  
Det 1 (CEEDO) ADTC/ECC  
Tyndall AFB FL 32403

The Environics Directorate (EC) of the Civil and Environmental Engineering Development Office (CEEDO) is the Air Force Laboratory focal point for environmental quality (EQ) research and development. In this capacity, CEEDO tracks the EQ related R&D efforts of all AF laboratories in addition to maintaining its own comprehensive multimedia (i.e. air, water, solid waste) program which includes R&D efforts in environmental modelling, chemistry, planning and monitoring as well as in resource conservation, control technology and energy research. Most of CEEDO's research is accomplished through industrial and university contracts many of which are jointly funded by organizations such as AFAPL, EPA, NASA and the Navy. Although CEEDO's major research thrust is in exploratory development (6.2) and advanced development (6.3) a limited amount of Laboratory Director's funds are available for basic research (6.1).

Since aircraft gas turbine engines burning military aviation fuels are a pollution source of special Air Force interest, CEEDO conducts R&D activities aimed to assure a fleet which meets Air Force aircraft engine emission goals and Federal, State, or local pollution regulations which affect military aircraft. Listed below are short descriptions of ongoing CEEDO research projects that most directly relate to aircraft engine emissions and combustion dynamics and kinetics:

a. Catalytic Combustor Development. The objective of this joint CEEDO/NASA Lewis program is to demonstrate an aircraft gas turbine engine main burner which employs catalytic combustion technology to achieve extremely low NO<sub>x</sub> emissions (<1gm NO<sub>x</sub>/kg fuel), at subsonic cruise. Pratt and Whitney and General Electric are currently under contract for Phase I, conceptual design and analysis. Ten candidate concepts are being considered; pending a go ahead by NASA and the Air Force, the two most promising concepts will undergo screening tests in FY79. This effort is fully described by Dr Larry Diehl elsewhere in these proceedings.



b. Variable Geometry Combustor Development. The variable geometry or air staging concept employs movable parts for regulating and varying the rate of airflow into various sections of the combustor. In effect the combustion zone equivalence ratio and local mass loading can be regulated. This fundamental characteristic has the potential to improve altitude relight, ground idle and starting problems and result in very low pollutant emissions. The variable geometry concept will be examined for application to military aircraft engine combustors in a joint NAPC/AFAPL/CEEDO contractual effort beginning early in FY79. The effort is described more fully by Capt R. M. McGregor and Dr R. Henderson elsewhere in these proceedings.

c. Fuel Character Effects Studies. It is inevitable that some changes in aircraft fuel specifications will be needed in the future in order to utilize alternate sources of crude stock and increase yields. However, before fuel specification are relaxed, the impact on engine combustor performance, pollutant emissions and combustor life must be known. To meet this AF need, the AFAPL and CEEDO began contractual fuel character effects studies late in FY77. In these parametric studies, up to thirteen fuel blends with varying hydrogen content, aromatic structure, volatility and distillation end point are burned in a variety of combustor types. This effort is fully described by Mr Martel et al elsewhere in these proceedings.

d. Microemulsions for Smoke Suppression. The Air Force has a continuing interest in controlling smoke emitted from jet engine test cells. Recently, the US Army Fuels and Lubricants Research Laboratory (AFLRL) located at Southwest Research Institute had success with low smoke, fire safe diesel fuel microemulsions in tanks. Microemulsions have the advantage of forming spontaneously if the proper emulsifying agent is present. In FY79 CEEDO will explore the possibility of JP-4 microemulsions and their application for smoke reduction in gas turbine engine combustors.

e. Automatic Isokinetic Jet Engine Sampler. The Navy and CEEDO have sponsored the development of an automatic isokinetic jet engine particle sampler. The sampler is undergoing evaluation at North Island Naval Air Station, San Diego. The fully automated sampler features a probe with a divergent supersonic inlet to allow isokinetic sampling up to Mach 1.4 and an electrical mobility aerosol analyzer for real time particle size analysis.

f. USAF Aircraft Engine Emission Goals. The Air Force aircraft engine emission goals established in the early 70's are the basis for CEEDO's involvement with low emission combustor development programs. Since then much has been learned about airport/airbase and stratospheric dispersion modelling of aircraft pollutants and about the limitations, development time, and costs of pollution reduction technology. In FY79 CEEDO will consider this new input in a reevaluation of AF emission goals.

g. Fuel Additive Evaluation. Both the Navy and the AF have demonstrated that fuel additives such as ferrocene can reduce smoke from gas turbine engines. This fall CEEDO, AFLC and NACP will sponsor evaluations of ferrocene and another iron based additive, XRG using a variety of engines at Tinker AFB. The engines tentatively included in the program are the J-57, J-75, TF-30, TF-33, and TF-41.

h. Fuel Additive Mechanisms. A survey of possible mechanisms for the action of smoke suppressant fuel additives was recently carried out for CEEDO by Professor Jack Howard of MIT. It does not appear that there is much hope at this time of finding any radically different smoke suppressant compounds. Moreover, the present understanding of soot formation and burn-out is extremely limited and more basic research is needed in this area.

i. Smoke Formation in Gas Turbine Combustors. To evaluate the impact of broadened fuel specifications on smoke emissions, CEEDO is sponsoring a new two year study by Dr Samuelsen of the University of California at Irvine. This study will be performed on a laboratory combustor, and will include optical as well as probe extractive measurements of smoke concentration and particle size. The effect of fuel properties and fuel additives will be considered.

j. Combustor Measurements at the Air Force Arnold Engineering Development Center (AEDC). AEDC, where the discrepancy between optical and probe measurements of NO was first noted, has been carrying out several studies for CEEDO. By taking measurements at several axial distances downstream of a combustor, they were able to show that the optical measurement of NO is conservative as the exhaust stream cools. CEEDO sponsored this study to determine whether the optical method correctly compensates for temperature effects. In another study funded by CEEDO and AFAPL, three different probe designs yielded widely different results for CO in a combustor exhaust. In a joint CEEDO/AEDC effort, a gas filter correlation spectrometer is being built to measure CO optically in the same combustor rig to determine which probe result, if any, it agrees with.

k. Interagency Investigation of NO. United Technologies Research Center is carrying out this program under joint CEEDO, EPA, FAA, NASA, and Navy funding. A thorough study of the measurement of NO in combustion exhaust, the program includes measurements of NO in cases ranging in complexity from a flat flame burner to the equivalent of a production engine combustor can. Measurements will be made using several different probe types and three optical systems. The first phase, calibration of the optical systems, is nearly complete, and probe design is underway. This program was prompted by reported discrepancies between probe and optical measurements of the same exhaust stream. Calibration measurements have led to the detection of some flaws in the previous optical measurements which may resolve part, but not all, of the reported disagreements.

l. NO Transformation in Heated Sampling Lines. This effort is being performed by Dr G. S. Samuelsen at the University of California, Irvine. CEEDO is funding this amplification of an ongoing AFOSR grant to permit the simulation of typical gas turbine engine exhaust conditions. This effort is fully described by Dr Samuelsen elsewhere in these proceedings.

m. Turbine Engine Exhaust Hydrocarbon Measurement by Gas Correlation Spectroscopy. This effort is jointly funded by CEEDO and the EPA and is being performed by Dr Darrell Burch of the Aeronutronic Division of Ford Aerospace and Communications Corporation. The development of a nonextractive optical method for measuring total hydrocarbons is complicated by the multiplicity of hydrocarbons present in turbine engine exhaust. It is hoped that the response of a suitably designed correlation instrument in a wavelength region where most hydrocarbons absorb (e.g. 0.3-3.5  $\mu$ ) can be related to the total hydrocarbon content measured by extractive FID response. A highly flexible gas correlation instrument is now being modified for this application; some preliminary high resolution spectra have been obtained.

n. Passive, Single Ended Measurement of CO. This study is also jointly funded with EPA and seeks to determine the important parameters for and limits of use of a single ended, passive gas filter correlation instrument to measure CO in turbine exhaust. As a passive system, its performance depends on the high temperature of the exhaust gases to act as a signal source, but it does not require the alignment of a separate source of radiation. Dr Chaney at the University of Michigan will perform this study with existing EPA instruments previously used only for double ended measurements.

o. Demonstration of the Measurement of Turbine Engine Emissions Using an Active Single Ended System. This Differential Absorption LIDAR (DIAL) system depends only on reflection of a laser signal off topographic targets of opportunity or the natural aerosol. Time gating of the reflected signal provides range resolved measurements, while absorption of the signal at two different wavelengths (on and off the absorbance of a given pollutant) gives the concentration. The system development and measurements will be performed by MIT's Lincoln Laboratory.

IONIC MECHANISMS OF CARBON FORMATION IN FLAMES  
CONTRACT NO. F49620-77-C-0029

W.J. Miller and H.F. Calcote

AeroChem Research Laboratories, Inc.  
P.O. Box 12, Princeton, NJ 08540

Problems associated with the formation of carbonaceous, particulate material (soot) in air-breathing engines will become more prevalent as "new fuels," i.e., those derived from coal, tar sands, and shale, come into more general use. The new fuels are characterized by more aromatic constituents, higher molecular weights, and higher C/H ratios than currently used, petroleum-derived fuels. All of these properties have been found empirically to enhance the smoking or soot-producing tendency of practical combustors. At present, there is not sufficient understanding of the basic chemical and physical processes associated with soot formation phenomena to make realistic predictions of the limiting conditions for its production or its effects on engine performance, heat transfer, plume structure or pollutant formation in Air Force missions. It is the objective of this program to provide information in the form of model chemical reaction mechanisms through which the desired predictive capabilities can be achieved and means for control developed.

The hypothesis being pursued in this investigation is one in which ions produced via chemi-ionization accompanying hydrocarbon oxidation serve as nuclei for the formation of incipient soot particles. A body of evidence in support of this theory had already accumulated prior to the start of this program and the work performed so far continues to indicate a close relationship between the appearance of soot and the formation of high molecular weight positive ions. The effects of fuel type, pressure, temperature, and chemical additives on both soot production and positive ion chemistry are being determined in laboratory test flames using electrostatic probes, optical diagnostics, and a direct sampling mass spectrometer.

Results reported at the last contractors meeting confirmed the highly critical effects of burner geometry, temperature, and flow rates on the threshold stoichiometry for the onset of soot formation. The annular Meker burner used in our studies produced flames which displayed the same general trends in critical equivalence ratios ( $\phi_s$ , the minimum fuel/air ratio for soot  $\div$  the fuel/air ratio at stoichiometry) as prior work using other burner configurations; more aromatic compounds and higher molecular weight fuels display greater tendencies to soot and pressure has little effect. Positive ion spectra of  $C_2H_2$ /air flames at 200 Torr and an equivalence ratio just short of  $\phi_s$  revealed a complex of species extending to above 300 amu apparently dominated in the mass range above 100 amu by ions with polycyclic naphthalenic and phenalenic structures.

Work since that meeting has produced ion spectra in 20 and 50 Torr  $C_2H_2$ /air flames actually exhibiting soot and in somewhat leaner  $C_6H_6$ /air flames for comparison. Electrostatic probe measurements have been made of total positive ion concentrations and their variations with distance through flames of several fuels. The approximate mass distributions of ions as functions of equivalence ratio have been determined for  $C_2H_2$  and  $C_6H_6$  flames and a correlation found between the ionic molecular weight and the mass loading of soot produced. Recently, investigations were begun into the sooting characteristics of fuel mixtures and the effects of chemical additives.

The charged species content of  $C_2H_2$  and  $C_6H_6$  flames display several features in common, as well as some important distinct differences. Spectra taken in both flames at fuel/air ratios very close to the point of soot onset,  $\phi_s$ , display striking similarity above 163 amu. The kinetics for producing larger molecular ions and thus soot forming nuclei must therefore be very much the same for acetylene and benzene beyond this point. It will be interesting to run a similar experiment with an alkane to see if it follows this same pattern. If so, then it will have been demonstrated that the ion chemistry that determines the difference in tendency to soot formation between fuels occurs in the very early stages of ion growth.

Below 163 amu the ion spectra are markedly different for acetylene and benzene. If the reasonable assumption is made that the only two elements in the molecular ions are carbon and hydrogen, then the C/H ratios of the ions produced in flames of these two fuels differ considerably. Thus:

C/H for ions unique to acetylene	1.72
C/H for ions in common	1.42
C/H for ions unique to benzene	1.03

Interestingly, C/H for the ions in common lies between the two fuels. An obvious interpretation of this data is that an aromatic molecular ion ( $C/H \leq 1$ ) must be formed to produce higher molecular weight ions. This is consistent with the observation that the observed changes in ion concentration and the appearance of soot as the equivalence ratio is increased are very abrupt for benzene flames and much less abrupt for acetylene flames. In the case of benzene, a molecule (or molecules) is present by which proton transfer can readily produce an aromatic molecular ion. In acetylene flames, the aromatic ion has to be first produced from smaller non-cyclic entities.

Many ions, particularly those of high molecular weight display two maxima in their concentration vs. flow time profiles in flames of either  $C_2H_2$  or  $C_6H_6$ . Electrostatic probe measurements of total positive ion concentrations confirm these mass spectrometric

observations of a second maximum and indicate that it is most apparent in flames on the verge of sooting, being less distinct in both richer and leaner mixtures. Similar effects have been observed in n-hexane, cyclo-hexane, and benzene flames. The downstream peak, when it appears, almost surely indicates the existence of a second ion formation region; changes in the ion/electron recombination rate, although they could explain changes in the slope of a decay curve, cannot account for an increase in the concentration vs. time profile. Whether the mechanism for ion formation is the same at both positions as in leaner flames is not clear at this time. Such questions will be explored in detail as our mechanistic interpretations are further tested by the results of future experiments.

# MECHANISMS OF EXHAUST POLLUTANT AND PLUME FORMATION IN CONTINUOUS COMBUSTION

G.S. Samuelsen

UCI Combustion Laboratory  
School of Engineering  
University of California, Irvine

## INTRODUCTION

The present analytical and experimental investigation is designed to clarify the relative influence of the mechanisms responsible for pollutant production in continuous combustion, develop and evaluate predictive methods for characterizing reacting flows, and assess experimental errors associated with sampling oxides of nitrogen. The research program encompasses studies of the physical and chemical processes contributing to pollutant and plume formation in jet engine continuous combustors. The results of the research will aid in establishing guidelines and techniques for reducing adverse environmental effects and controlling plume signatures in present day and advanced jet engine combustors by control and modification of the combustion dynamic processes.

Combustion experiments are being conducted with both nonreacting and reacting laboratory combustors under conditions simulating the basic flow characteristics of gas turbine engines. In addition, theoretically predicted profiles of the flow properties are being compared with experimentally determined profiles to evaluate the predictive methods used to solve the governing differential equations and the associated models of turbulence and chemical kinetics for reacting flows. Deficiencies in present models are being identified and used to refine the predictive methods with the goal of accurately predicting the formation of combustion generated pollutants.

Sampling experiments are being conducted with simulated combustion products at concentrations representative of primary and secondary zones of gas turbine combustors, and exhaust planes of gas turbine engines. Conditions for which changes occur in oxides of nitrogen concentration and composition during sample extraction and sample transport are being identified and used to refine the experimental methods with the goal of accurately measuring combustion generated pollutants.

## RESULTS

The evaluation and development of predictive methods have emphasized the performance of predictive methods in describing mass and momentum transport in recirculating flows in the absence of reaction. The turbulent flowfield of an atmospheric backmixed combustor has served as the vehicle for examination. The configuration is a turbulent



pipe flow with an on-axis jet opposing the main flow. Mass transfer is explored by introducing a tracer species (carbon monoxide) through the jet and observing the axial and radial mass transport. Momentum transport is evaluated by comparison of experimentally measured profiles of velocity and turbulent kinetic energy to those predicted. It has been earlier shown that boundary conditions for eddy dissipation rate in the vicinity of the recirculation zone dramatically influence the predicted mass and momentum transport. The present study demonstrates that transport characteristics are also strongly influenced by (1) the coefficients in the source and sink terms of the turbulence energy dissipation rate equation, and (2) the specification of turbulence kinetic energy at the jet inlet.

The reacting flow studies have focused on internal flowfield measurements of species composition and temperature. The opposed-jet combustor has been operated for a range of main and jet stream velocities and equivalence ratios to assess the effect of recirculating zone mixing and intensity on pollutant formation. The data also provide an experimental base against which predictive modeling can be tested.

The sampling experiments have addressed the effect of sample line surface condition on the change to nitrogen oxides composition and concentration during transport. Stainless steel tubes ( $\frac{1}{8}$ -inch O.D.) that are preoxidized or prereduced are found to change the extent of chemical change. The early results indicate that the change (1) depends upon the extent of prereduction or preoxidation, and (2) is not permanent but reverts to the performance of an unconditioned probe within thirty minutes of operation.

FUNDAMENTAL COMBUSTION STUDIES  
RELATED TO AIR-BREATHING PROPULSION

F. A. Williams

Professor of Aerospace Engineering  
Department of Applied Mechanics and Engineering Sciences  
University of California, San Diego  
La Jolla, California 92093

The overall objective of this research is to develop further basic knowledge in combustion that will be useful for improving efficiencies and operating characteristics of propulsion units. During the past year work has been performed on theory and experiment involving combustion of droplets and of carbonaceous particles and on the theory of turbulent combustion. The first of these topics is relevant to combustion efficiencies and smoke emissions from air-breathing combustors. The second bears on flame stability, combustion efficiency and the range of useful operating conditions for air-breathing engines.

In the area of droplet and particle burning, progress was made on setting up an optical multi-channel analyzer to make spectrographic measurements of burning droplets and particles on a time-resolved basis, largely for the purpose of testing the gray-body assumption employed in earlier work based on two-color optical pyrometry. Ignition theory has been developed for ignitions by a constant surface temperature. In addition, further progress has been made on the theory of surface oxidation of carbon, but uncertainties remain in the results. Turbulent combustion theory produced formulas for the flame speed for large-scale turbulence and clarified the wrinkled laminar flame description of turbulent flame propagation. The presentation will be restricted to this last topic, in which the greatest amount of progress has been made.

A statistical theory was developed for the structure and propagation velocity of premixed flames in turbulent flows having scales large compared with the laminar-flame thickness. The analysis, free of usual closure assumptions, involves a regular perturbation for small values of the ratio of laminar-flame thickness to turbulence scale termed the scale ratio,  $\epsilon$ , and a singular perturbation for large values of the nondimensional activation-temperature,  $\beta$ . Any effects of the flame on the flow are considered to be given. In the initial study, molecular coefficients for diffusion of heat and reactants are set equal. The results identify convective-diffusive and reactive-diffusive zones in the flame and predict thickening of the flame by turbulence through streamwise displacement of the reactive-diffusive zone. Profiles for intensities of temperature fluctuations and for streamwise turbulent-transport were obtained.

A fundamental quantity occurring in the analysis is the longitudinal displacement of the reactive-diffusive zone in an Eulerian frame by turbulent fluctuations, and to first order in the scale ratio this equals the longitudinal displacement of fluid elements in an Eulerian frame by turbulent fluctuations, herein termed simply the Eulerian displacement. To first order in scale ratio it was found that if the Eulerian displacement experiences the same type of statistical nonstationarity as the corresponding Lagrangian displacement, then the diffusion approximation is valid for streamwise turbulent-transport but the turbulent flame thickens as time increases, while if the Eulerian displacement is statistically stationary then the diffusion approximation would necessitate a negative coefficient of diffusion in part of the flame but the flame thickness remains constant.

By carrying the analysis to second order in the scale ratio it was shown that the turbulent flame-speed exceeds the laminar flame-speed by an amount proportional to the mean-square value of the transverse gradient of the Eulerian displacement. This result can be understood from the mechanistic viewpoint of a wrinkled laminar-flame in terms of increase of flame area produced by turbulence. Thus, the theory provides a precise, statistical quantification of the model of the wrinkled laminar-flame for describing the structures of turbulent flames.

Follow-on work has involved consideration of effects of the Lewis number for the deficient reactant differing from unity. It recently was found that in this case there is an influence on flame speed, beyond that discussed above, due to fluctuations of the flame temperature as a consequence of unequal fluctuating diffusion of reactant and heat, in response to the fluctuating velocity field. The resulting additional flame-speed correction appears to involve the Taylor scale.

AIR FORCE AERO PROPULSION LABORATORY FUELS COMBUSTION PROGRAM  
AFAPL/In House

Charles R. Martel

Department of the Air Force  
Air Force Aero Propulsion Laboratory (AFSC)  
Wright-Patterson AFB, OH 45433

The mission of the Fuels Branch, Fuels and Lubrication Division, Air Force Aero Propulsion Laboratory, is to conduct the necessary research and development needed to insure the supply of aviation turbine fuels of adequate quantity and suitable quality. This mission was relatively straightforward when petroleum-based aviation turbine fuels could be provided in adequate quantities to meet peacetime and wartime requirements. However, as emphatically demonstrated by the Arab oil embargo of 1973, adequate quantities of petroleum-based fuels can no longer be assured even in peacetime.

Beginning in 1974 the Fuels Branch initiated an alternative fuels program to investigate other fossil resources such as oil shale, coal, and tar sands as potential sources for aviation turbine fuels. The actual production and refining of such fuels would, of course, remain a commercial enterprise. However, to be able to prepare adequate specifications for aviation turbine fuels derived from low-quality petroleum and nonpetroleum sources, extensive research, development, and testing are necessary to determine the optimum fuel properties that assure adequate fuel quality at minimum fuel cost.

The Fuels Branch alternative fuels program consists of several technical areas, one of which is fuels combustion. The objective of the combustion program are: (1) to determine the fuel properties that significantly affect the combustion performance of existing and future aircraft turbine engine combustors; (2) to determine the magnitude and importance of these effects on combustor performance and durability; and (3) to identify possible combustor modifications that would increase the capability of existing and future combustors to burn lower quality fuels.

Other related alternative fuel programs include: (a) Processing Studies - to determine the costs involved in upgrading low quality fuels to higher quality fuels; (b) Fuel Analysis Methods - to accurately define the composition and properties of candidate and test fuels; and (c) Economic Studies - to conduct trade-off studies of fuel processing costs versus aircraft engine maintenance and retrofit costs to select the fuel properties that provide the lowest life cycle cost for Air Force systems. This total alternative fuels program has been coordinated with other DoD agencies and with a similar NASA program for commercial aviation fuels. Key differences between commercial aviation requirements and the military requirements may result in significant differences between future military aviation fuels and commercial aviation fuels.

Another major program area in the Fuels Branch concerns fuels for air-breathing missiles, both ramjet and turbine engine powered. As these missiles are normally volume limited, i.e., fuel capacity is determined by volume restraints, not weight restraints, fuels having a high volumetric heat of combustion are required. JP-9 and JP-10 fuels are two recent developments of the Fuels Branch that give a 20% greater volumetric heat of combustion than JP-4. Future missile fuel programs will investigate carbon and metal slurry fuels. Significant combustion research may be needed if the potential performance of slurry fuels is ever to be realized.

The Fuels Branch and the Fire Protection Branch of the Fuels and Lubrication Division currently sponsor five basic research programs in the fuel combustion area. A contract with Exxon Research and Engineering, jointly sponsored by the Department of Energy, is investigating fuel pyrolysis. An in-house program with contractor support from Purdue University is underway to validate mathematical models of combustion. A combustion diagnostics program with the University of Dayton Research Institute is tied into the combustion model validation program. Two programs to help prevent unwanted combustion in aircraft, one with the University of Dayton Research Institute and the other with Exxon Research and Engineering Company, are also underway. All of these programs will be discussed in detail by the appropriate project scientist or contractor.

FUNDAMENTAL CHARACTERIZATION OF ALTERNATE  
FUEL EFFECTS IN CONTINUOUS COMBUSTION SYSTEMS

W. S. Blazowski  
Exxon Research and  
Engineering Company  
Linden, New Jersey

R. B. Edelman  
Science Applications, Inc.  
Woodland Hills, California

### Introduction

Alternate fuels derived from coal, oil shale, and tar sands are expected to play an increasingly important role in meeting the future national energy demand. The properties of these fuels can result in significantly different combustion performance compared with conventional specification fuels. For example, decreased hydrogen content can result in increased flame luminosity and exhaust smoke emission, higher fuel bound nitrogen can result in increased  $\text{NO}_x$  emissions, and fuel impurities can result in deposition within the combustion device. Although additional refining and fuel treatment can mitigate these problems to some extent, the approach of adapting the combustion system to utilize fuels having "unconventional" properties while operating in an environmentally acceptable manner seems to be most cost effective and energy efficient. This program will provide vital fundamental information necessary for the efficient pursuit of this approach.

The subject program is a multi-year effort with two primary objectives: a) to provide an improved understanding of the relationships between fuel properties and combustion characteristics and b) to develop analytical modeling/correlation capabilities for the prediction of fuel effects. The work will be limited to investigation of alternate liquid fuels used in continuous combustion systems, with gas turbine systems receiving special attention. Future electric power generation with combined cycle gas turbines makes it imperative that technology be developed to allow operation on liquid synfuels with minimum refining. Development of such a fuel-flexible gas turbine will have major impact on future conservation of petroleum supplies and on the cost of power production. The results of this program will also benefit the second important gas turbine application, aircraft propulsion. In this case, the future use of lower hydrogen content fuels can improve availability (a vital consideration for military applications) and reduce cost.

The program philosophy is to relate fundamental combustion phenomena to fuel characteristics using analytical models developed with and eventually verified by data obtained in carefully designed experiments. Figure 1 describes this approach schematically. The model can be envisioned as a combination of chemical and fuel related elements, thermodynamic and heat transfer elements, and gas phase elements. A solution scheme provides the mathematical procedures for solving the many complex mathematical relationships. The subject program focuses on the fuel related elements appearing in the upper left portion of the schematic but includes devoting sufficient attention to other elements to result in the development of a successful model. The program will proceed along two parallel, strongly-interactive paths involving both modeling and experimental tasks. ER&E will be responsible for overall program direction and experimentation, while Science Applications, Inc. (SAI) will be responsible for analytical modeling undering subcontract to ER&E.

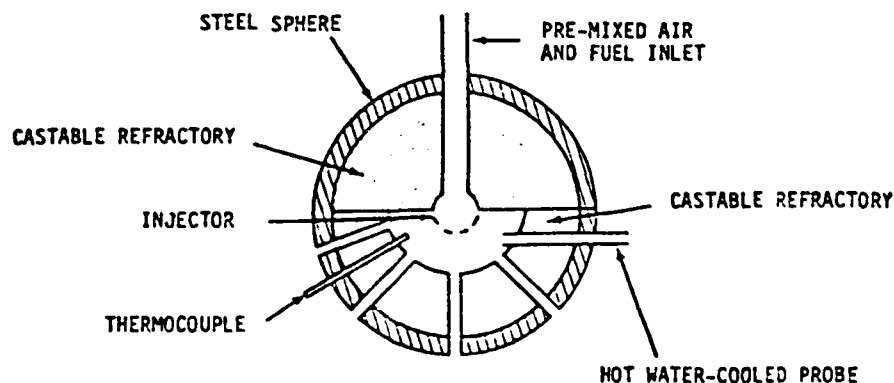
Effort during the first phase of this program (August 15, 1977-September 30, 1978) provided a well-developed plan for subsequent years of the program. Key combustion properties and ranges of fuel variation of interest to our subsequent efforts were surveyed. Experimental work included utilization of the Jet Stirred Combustor for evaluation of fuel combustion characteristics. The analytical modeling effort included new applications of quasi-global modeling techniques as well as predictions of and comparisons with the experimental results generated.

#### Experimental Program Status

The first year experimental program focused on study of the soot formation process using the Jet-Stirred Combustor (JSC) shown schematically in Figure 1. This device provides very rapid mixing of an incoming fuel-air mixture and the combustion products within the reactor. It has been used extensively in the study of combustion chemistry because combustion rates are limited by chemical kinetics as opposed to mixing or transport effects. A key advantage of the JSC for the present program is that the strongly backmixed nature of the combustion process occurring in the JSC provides a simulation of the recirculating characteristics of the gas turbine primary zone. It is in this region where mixture conditions are sufficiently rich to produce soot. Consequently, the JSC allows study of soot formation in an aerodynamic situation relevant to gas turbine systems. Another advantage of the stirred combustor is that the reactor is homogeneous in species concentration as well as temperature; each operating condition is characterized by a single set of temperature and concentration data rather than profiles of these parameters. This simplifies the tasks of obtaining and interpreting the data.

FIGURE 2

#### The Jet Stirred Combustor



The following conclusions have been drawn from the first year experimental effort.

- Ethylene and toluene have distinctly different soot formation characteristics in backmixed combustion.
- The hydrocarbon concentration at and beyond the incipient soot limit appears to be a dominant factor influencing sooting characteristics.
- Other hydrocarbons may be categorized as like-C<sub>2</sub>H<sub>4</sub> or like-C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> with 1-methyl-naphthalene being a more powerful soot-producing compound.
- Fuel blend testing indicates a combination of like-C<sub>2</sub>H<sub>4</sub> and like-C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> behavior.
- Results provide encouragement for our initially-proposed approach of generating quasi-global soot formation models for categories of hydrocarbons.

#### Analytical Modeling Status

The objective of the analytical portion of this program is to develop an engineering model of continuous flow combustors for design and advanced concept evaluation that is sensitive to alternate fuel properties. The experimental results developed in this program as well as information available from other sources will be utilized in developing the model.

The method of approach has two facets. The first involves the selection of a model framework which can accommodate the coupling of physical and chemical mechanisms relevant to continuous flow combustors of the gas turbine type. The second involves the development of models that characterize the physical and chemical mechanisms. The model accommodates turbulent recirculating flows with swirl coupled to the physicochemical processes of fuel pyrolysis and oxidation, soot formation and oxidation, and droplet and spray dynamics and combustion.

To date, a state-of-the-art assessment has been completed and is described in the first quarterly report of this program, a modeling approach has been established, and the application of data obtained from the jet stirred reactor to kinetics model development has been initiated. The modeling approach selected is based on the modular model concept, in which discrete parts of the flow, such as recirculation zones, jet-flow regions, shear layer regions, and fuel injection regions are each characterized in different elements, or modules of the overall model. Each module is treated in detail. For example, a two-dimensional treatment is used to describe the jet flow region and a well-stirred reactor model is used to characterize the recirculation region with advanced turbulence modeling to characterize the shear stress in the jet flow region and the unmixedness in the stirred reactor region. The modules are interactively coupled through their boundary conditions. The gradients of chemical species, mean energy and turbulent kinetic energy established in the shear layer module which bound both the jet flow and recirculation modules may establish the feed rate of these quantities into the recirculation zone. In both the jet flow and recirculation zone regions, chemical kinetics is characterized by a multistep quasi-global model accounting for pyrolysis, soot formation, and oxidation.



Application of JSC data to kinetics model development during this first program year involves prediction of CO mole percent at lean operation and hydrocarbon composition at fuel rich conditions. Carbon monoxide prediction using the current quasi-global model are within a factor of two of all the data shown over the equivalence ratio range of the data. Furthermore, both the data and the predictions show the existence of a characteristic minimum in the CO mole percentage, which can be a sensitive indicator of the behavior of the chemical kinetic model used in the prediction. Hydrocarbon predictions using the current quasi-global model also appear to follow the experimentally-determined trends but quantitative agreement is not as good as in the case of CO.

THREE DIMENSIONAL ABSORPTION DIAGNOSTICS  
CONTRACT NO. AFOSR-77-3439

P. Emmerman and R. Goulard

SEAS/SMEF  
The George Washington University  
Washington, DC

The applicability of tomographic reconstruction algorithm to combustion measurements is governed by the dynamics of the system under test. Meaningful two dimensional distributions of absorption coefficients can only be obtained if the aperture time of the measurement is small compared to the time required for significant change of the measured quantities. This time limitation which may be of the order of milliseconds or even microseconds severely constrains the number of projections available for reconstruction. Most tomographic algorithms are excellent at reconstructing the types of functions expected in unconstrained combustion if provided sufficient projection data. Because of these time constraints it is necessary to examine and optimize these algorithms with respect to using a minimum number of projections.

The convolution algorithm was chosen as the primary means to analyze the reconstruction of a variety of symmetric and non-symmetric, continuous and discontinuous functions. This algorithm, which is representative of the class of Fourier based reconstruction techniques, has the advantages of speed of implementation and of being analytically tractable. A comparison is made between the Fourier based algorithms and the iterative algebraic reconstruction techniques. Test functions composed of two dimensional Gaussian fields represent the anticipated distribution in an unconstrained combustion process. Constrained combustion processes are approximated by a summation of cylindrical and Gaussian functions.

A rough qualitative evaluation of Gaussian functions can be obtained with as few as two equally spaced curves. To ascertain an accurate reproduction of these functions (error in the order of 1%), ten equally spaced projections are sufficient. If reconstruction error in the order of 10% (particularly in the periphery of the spatial domain) can be tolerated, as few as five projections are sufficient. Filtering and additional processing were implemented to improve the reconstruction. Filtering had negligible effect on the error magnitude. Correlation between the reconstruction results of three and six projections offers some improvement. As would be expected, functions which have discontinuities are much more difficult to reconstruct, although proper filtering has a large effect on the accuracy of the reproduction. Small amplitude Gaussian distributions easily become obscured by the ringing caused by these discontinuities. To be able to limit the number of projections necessary (<50) for a reasonably accurate reconstruction, significant preprocessing of the data shall be required.

Therefore, in terms of practical flame applications, there seem to be two areas of useful absorption diagnostics. One is for three dimensional real time measurements of low concentrations from a [laser - 5 beam splitters - 5 sensors] combination, provided the flame profiles are smooth. The other is for three dimensional time-averaged measurements of arbitrarily complicated cylindrical sets of low concentrations, following the well proven techniques of X-ray tomography and material analysis.

Experimental Investigations of Reacting Flows in Practical  
Air-Breathing Engine Combustion Environments Utilizing  
Advanced Diagnostic Techniques.

W. M. Roquemore and Paul W. Schreiber

Air Force Aero Propulsion Laboratory

Introduction

An improved understanding of combustion processes can be obtained through the experimental characterization of combustion media. Optical techniques are attractive because they often permit in-situ measurements (with spatial and temporal resolution) of such parameters as gas temperature, species concentration, and flow velocity, without introducing any disturbance to the processes being studied. On the other hand, probes are rugged, inexpensive, and relatively easy to use; hence, they will remain the standard techniques for combustion research.

The Air Force Aero Propulsion Laboratory (AFAPL) has a combination of in-house and contractual programs in which the feasibility of using conventional probes (Ref. 1), spontaneous Raman scattering, (Ref. 2), coherent anti-Stokes Raman scattering (CARS) (Ref. 3), two-line fluorescence (Ref. 4), and laser Doppler velocimetry (LDV) (Ref. 2), techniques in different combustion environments are being evaluated. The promising techniques will be used in common experiments in AFAPL's combustion tunnel to collect data for evaluating combustor models. The program is in the diagnostic evaluation phase. The next sections summarize the latest results obtained with probes, Raman, and CARS techniques. The LDV and the two-line fluorescence techniques are in a very early stage of development on our contracts and will not be discussed. The combustion tunnel is in a "debugging" phase and also will not be discussed.

Comparison of Raman, Gas Sampling and Thermocouple Temperatures

A study was performed to assess the feasibility of using spontaneous Raman scattering to measure temperatures in the plume of an afterburning J85-5 turbojet engine (Ref. 5). This assessment required Raman spectral measurements of sufficiently good quality to permit temperature determinations and confirmation that the temperatures were correct within reasonable error limits. Our basic approach was to use gas sampling as a standard technique to be compared with the Raman technique. Simultaneous gas sampling and Raman measurements were made at about the same time and location in the plume (114 cm from nozzle exit plane) and for different engine afterburning conditions. Additional gas sampling measurements were made later in the test program along with thermocouple measurements. Raman, gas sampling, and thermocouple measurements were then compared by plotting temperature rise versus engine fuel-air ratio. Some of the results and conclusions from these measurements are summarized below:

(1) Raman N2 Q-branch spectra were obtained with sufficient resolution to permit temperature measurements over the entire operating range of the after-burner. The temperatures were determined by fitting theoretical spectral profiles to experimental data.

(2) The error in the Raman temperatures estimated from the spectral-profile fitting procedure, varied between about 1% and 4% depending on test conditions. These errors may be a little low but appear reasonable based on the comparisons with other techniques.

(3) Simultaneous Raman and gas sampling temperatures agreed with experimental error of about 3%.

(4) Engine static temperature rise was measured by Raman, gas sampling, and thermocouple techniques over an engine F/A ratio range of 0.017 to 0.052. A plot of these data versus engine F/A ratio showed that the three techniques agreed within about 5%.

(5) Laser induced background, believed to be due to fluorescence, was the major contributor to errors in Raman temperatures.

(6) The feasibility of making Raman measurements at other spatial locations in the J85-5 plume and in other combustion environments cannot be predicted a priori because of the uncertain nature of the laser induced background.

#### Coherent Anti-Stokes Raman Scattering (CARS)

The major objectives of the CARS program are: (1) to establish the parameter space for the application of CARS and (2) to develop and evaluate a hardened CARS system for in-situ measurements in AFAPL's combustion tunnel.

A technique, which is presently being used by other laboratories, was developed which allows the simultaneous generation of the entire Q-branch spectrum of the CARS radiation from a molecular gas to be recorded for a single laser pulse. The excellent temporal resolution (20 nsec) makes this technique very attractive for temperature and concentration measurements of molecular gases in turbulent media (Ref. 6). In addition, the pressure dependence of the integrated CARS power in a Q-branch has been investigated. CARS power was found to be inversely proportional to linewidth in contrast to spontaneous Raman scattering for which the integrated power is independent of linewidth. This effect makes the measurement of species concentrations more difficult, and analytical as well as experimental methods need to be developed to correct for this effect. Experimental effects of pressure were obtained for CH<sub>4</sub>, CO, N<sub>2</sub> and H<sub>2</sub>. In addition, the effect of Doppler broadening on the integrated power of CARS has been studied theoretically. A relativistic treatment shows that the integrated CARS power is also inversely proportional to the linewidth as in the case of the pressure-broadened regime. Linewidths obtained from the integrated power of the Q(1) line of H<sub>2</sub> are in good agreement with resolved spectra (Ref. 7,8). The effect of turbulence on the generation of CARS has been investigated experimentally and theoretically. If instantaneous spectra can be obtained, turbulence should not effect temperature measurements. For long paths through highly turbulent media, a decrease in the CARS signal occurs; and this effect can cause errors in number density measurements. Methods to minimize the turbulent effects and to correct the data are under investigation. Preliminary

temperature and species concentrations have been measured in a laminar flat flame burner and compared with data based on thermocouple and mass spectrometric probes. At present, the use of hot bands of CO<sub>2</sub> to measure vibrational temperatures is under investigation. This appears to be a promising technique since data collection and data analysis is simplified.

A hardened CARS system has been designed, fabricated, and tested in the laboratory. This system has a pulse repetition rate of one pulse per sec and is similar in design to the laboratory system. In addition, the output from the photomultiplier may be recorded on tape and number densities can be calculated for each pulse. This CARS system will be used to make in-situ species and temperature measurements in the combustion tunnel facility at AFAPL.

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INVESTIGATION OF LASER INDUCED  
FLUORESCENCE SPECTROSCOPY FOR MAKING  
IN-SITU SPECIES CONCENTRATION MEASUREMENTS  
IN TURBULENT COMBUSTION FLOWS  
AFOSR-77-3357

John W. Daily

University of California  
Department of Mechanical Engineering  
Berkeley, California 94720

The study of reacting gas flows has traditionally been limited by a lack of experimental data. The measurement of temperatures and species concentrations in complex flames with sufficient spatial and time resolution would be especially desirable. Under AFOSR Grant 77-3357 we have been investigating the application of saturated Laser Induced Fluorescence Spectroscopy (LIFS) to measurement of species concentrations in flames.

The LIFS method consists of illuminating the gas with a pulsed laser tuned to an absorption line of the species of interest. The species is excited and fluoresces. The fluorescence is observed at 90° to the laser beam, the volume formed by the intersection of the laser beam and the collection optics defining the spatial resolution. If a relationship between the number density of the fluorescing states and the total number density can be found, then the fluorescence is a measure of the total number density. Saturation usually simplifies the relationship. Furthermore, if a measurement can be made with a single pulse then turbulent measurements are possible. Preliminary work with sodium has demonstrated the feasibility of saturated LIFS for atomic species. We are now working on diatomic radical species, concentrating on OH.

Diatomic molecular present difficulties not found with atomic species. Because of the large number of rotational/vibrational sub-levels available in both the ground and excited electronic states, the nature of rotational relaxation has a strong influence on the fluorescent signal. Although saturating the pumping transition provides some simplification, only in certain limits will the fluorescence signal be unambiguously related to the total number density.

We are now conducting experiments and performing an analysis to study the effects of relative energy transfer rates. For example, it has long been believed that the rotational relaxation rates are much faster than the collisional quenching rates, and that the excited OH molecules should be at rotational equilibrium long before decaying to the ground state. Therefore, we should expect the fluorescence spectrum to look similar to the emission spectrum. Surprisingly, this may not be the case. We will show several fluorescence spectrum which represent the situation where quenching is much faster than rotational re-distribution. We will

also discuss how pumping and detection strategy can be used to simplify measurements.

In addition to the above work we will discuss two other subjects which have arisen from our studies. 1) Near resonant Rayleigh scattering offers a unique solution to the problems encountered in atomic fluorescence spectroscopy in the optically thick limit. 2) The use of LIFS may allow the study of excited state chemistry for both atomic and molecular species in flames.



COMPARISON OF RAMAN SCATTERING METHODS  
FOR COMBUSTION DYNAMICS MEASUREMENTS

M. Lapp, Principal Investigator  
C. M. Penney, Physicist  
S. Warshaw, Physicist

General Electric Company  
Corporate Research and Development  
P.O. Box 8, Schenectady, NY 12301

Although steady progress has been made through the years in the development and refinement of air-breathing combustion devices, current demands of a severe nature on many of these devices severely stress the traditional methods for making these improvements. A cornerstone of efforts to improve this situation is the attempt to achieve an increased understanding of detailed fluid mixing processes, flame chemical reactions, turbulence properties, etc., for which current experimental data and analytical insight are either incomplete or substantially lacking.

In our approach to contribute to the solution of this problem, we are focussed upon the achievement and critical comparison of improved measurement methods--in particular the experimental exploitation of vibrational Raman scattering (VRS) for temperature diagnostics, and the analytical comparison of these results with analogous diagnostic capabilities of another promising light-scattering probe, coherent anti-Stokes Raman spectroscopy (CARS), whose capabilities are under investigation presently at AFAPL.

Carefully-designed burners for producing laminar premixed and turbulent diffusion flames are being utilized to produce reproducible combustion configurations, and VRS (and CARS, at AFAPL) techniques will be applied to measure instantaneous values of temperature at a variety of locations. Specific experimental difficulties, such as luminosity (more difficult for VRS) and high levels of turbulence (more difficult for CARS), will be introduced in a logical progression in order to evaluate these methods.

We will discuss the first year's work in this effort, which has been concentrated upon tasks related to burner exploration and selection, the preliminary testing of representative configurations of these burners, and exploration of the limitations of Raman temperature measurement accuracy that can be achieved for relatively clean flames.

We are presently obtaining VRS fluctuation temperature data for an interim modified version of our original fan-driven co-flowing turbulent combustor, while we are in the process of design and fabrication of a significantly-improved new combustor. This new facility will have fan-induced flow, and will have many potential experimental

advantages over the earlier devices (for example, through improved experimental rigidity, greater attention to fuel-tube boundary layer effects, careful control of flow turbulence at the fan-induced air inlet, flexible optical access conditions, etc.).

In exploring the limits of VRS temperature accuracy, we have studied (1) the accuracy of the present VRS scheme based upon Stokes/anti-Stokes intensity ratios, both experimentally (with a laminar flame "isothermal" test zone) and analytically, achieving standard deviations of 5-7% by independent methods for fluctuation temperatures with our initial set-up. Through these calibrations, we have obtained a temperature "spread function", which permits us to estimate experimentally-introduced temperature data scatter, in order to better quantify subsequent turbulent temperature histograms. (2) We have also explored limiting fluctuation temperature measurement difficulties for relatively clean turbulent flame conditions for VRS, finding that substantial care must be taken in treatment of residual levels of background signal - either originating from luminosity or from spurious electromagnetic generation of signals somewhere in the electronic detection apparatus. These uncertainties have now been decreased to a relatively low level, but care must be taken continually to prevent the possible introduction of consistent errors in data analysis from such causes.

DEVELOPMENT OF TUNABLE LASER ABSORPTION SPECTROSCOPY  
AND APPLICATIONS TO STEADY AND FLUCTUATING COMBUSTION FLOWS

AFOSR F49620-78-C-0026

R. K. Hanson and C. T. Bowman

High Temperature Gasdynamics Laboratory  
Mechanical Engineering Department, Stanford University  
Stanford, California 94305

1.0 Introduction

Increasing demands on Air Force combustion systems have stimulated new interest in combustion processes and in the development of new laser-based diagnostics for combustion studies. This presentation will describe work underway at Stanford to develop and apply tunable infrared diode lasers for measurements in steady combustion flows. Future research plans, involving application of the diode laser to studies of fluctuating or turbulent combustion flows also will be discussed.

Tunable infrared diode lasers are well-suited for in situ absorption spectroscopy measurements of species concentrations and temperature in combustion gases. These lasers are also a powerful tool for determining spectroscopic parameters needed to describe the spectral characteristics of radiation from high temperature gases, such as found in engines, exhausts and plumes. The diode laser serves as a source of narrow-linewidth ( $10^{-5}$  cm $^{-1}$ ) infrared radiation whose wavelength can be rapidly modulated ( $> 10^{-3}$  cm $^{-1}$ /microsecond) to perform fast, high-resolution absorption spectroscopy. The complete fully-resolved absorption profile of an individual vibration-rotation line can thus be quickly recorded, and from this one can infer the partial pressure of the absorbing species and the lineshape parameters describing the absorption line. Temperature can also be determined by measuring the relative absorption in adjacent lines originating from different vibrational levels. Diode laser absorption spectroscopy also should be applicable to two-phase flows in that modulation of the laser wavelength on and off an absorption line should provide discrimination against beam blockage effects. The ability to rapidly modulate the laser suggests that diode laser techniques can also be applied to studies of transient combustion phenomena.

Advantages of tunable diode laser absorption spectroscopy are its simplicity, high sensitivity, high spectral resolution (orders of magnitude improvement over conventional ir spectroscopy), and fast modulation capability. The primary limitation, for some applications, is that it is a line-of-sight method. In this first

year of our research program we have demonstrated the feasibility of diode laser techniques for measuring CO species concentrations and temperature in a steady flat flame combustion system. Work is now in progress to extend these measurements techniques to both a fluctuating flat flame and a time-dependent 2-dimensional shear layer.

## 2.0 Results

During the past year, experiments have been conducted in the steady postflame region of a laminar, premixed, flat-flame burner operating at atmospheric pressure. Measurements of temperature and CO species concentrations have been made using tunable diode laser absorption spectroscopy to demonstrate the utility of this combustion diagnostic technique. The measurements involve rapidly scanning the narrow-linewidth diode laser across individual vibration-rotation absorption lines in the 4.6 micron fundamental band of CO to record fully-resolved absorption line profiles. This information (obtained in times as short as 50 microseconds) has been used to infer both gas temperature and the concentration of CO. A conventional microprobe sampling system to monitor CO and CO<sub>2</sub> concentrations also have been constructed to enable comparisons between laser-based and conventional measurements; thermocouples have been used to allow comparisons with laser-based temperature measurements. Initial results in fuel-rich propane-air flames show good agreement. Work is in progress to modify the burner system to allow comparisons over a wider range of stoichiometries.

During the past few months we have also begun design of two new facilities for studies of the dynamics of fluctuating or turbulent combustion flows. The first facility is essentially a flat flame burner modified to provide repetitive fluctuations in flame gas stoichiometry and temperature. Our approach will be to make spatially-and temporally-resolved measurements of species concentrations (CO or NO) and temperature in the post-flame flowfield and to compare these with a theoretical model incorporating coupled fluid mechanics and kinetics. The second facility, now under construction, is a two-dimensional reacting shear flow facility. The intent is to study the coupling between fluid dynamic and chemical processes associated with the presence of large-scale, organized structures. The selection of the two-dimensional geometry should enable use of line-of-sight optical techniques including diode laser spectroscopy.

COHERENT STRUCTURES IN TURBULENT FLAMES  
BY LASER ANEMOMETRY

Norman A. Chigier

University of Sheffield, England

The main objective is to develop more sensitive, selective, precise, reliable and rapid diagnostic methods for measuring important parameters in jet engine reacting flow environments; to utilize laser Doppler anemometry for obtaining high frequency and time resolution velocity measurements and also particle size in practical combustion environments. The main emphasis is being placed on accurate measurement of velocity, temperature and their correlations in mixing regions of turbulent jet flames. A further aim is to provide reliable experimental data for use by combustion modelers.

The specific approach to this study is the utilization of laser anemometry and fine wire thermocouples for measurement and detection of coherent structures in turbulent diffusion flames. The high frequency response laser anemometer, powered by an argon ion laser and single particle counter, interfaced with a high-speed computer, provides information on variation of velocity with both space and time. Growth and movement of coherent structures are studied by high-speed movie-photography and these are related to direct measurement of velocity and temperature. The detailed physical mechanisms of fuel-air mixing across interfaces will be studied and related particularly to presence of large eddies and coherent structures in the turbulent flow field. The effect of impingement of a turbulent jet flame on a cold flat plate will be studied to show the extent to which coherence of eddy structures can be maintained after jet impingement. Initially, efforts will be concentrated on the development of the diagnostic techniques and the making of measurements in gaseous diffusion flames. At a later stage, heterogeneous combustion will be studied, using liquid sprays.

An experimental study is being carried out on the structure of turbulent propane/air diffusion flames. Measurements have been made in the mixing region of an axisymmetric turbulent propane/air jet issuing from a round nozzle into a low-velocity, low-turbulence intensity, unconfined coflowing airstream. The exit velocity of the jet fluid and its turbulence intensity are sufficiently low to allow the formation of ring vortices within the mixing layer, bounded, on the inside, by the potential core of the jet and, on the outside, by the secondary airstream. A Hadland scientific movie camera, at 10,000 frames per second, shows evidence of formation of eddies and flamelets and their change in shape and movement downstream of the nozzle exit. Within the flame, 'instantaneous', 'point' measurements of velocity variation are measured by a single particle-counting forwardscatter laser anemometer. Si O<sub>2</sub> seeding particles are

added to the central burner and the secondary flow. Some measurements are also made with in situ local seeding particle injection. Temperature variation with time is measured with micro-thermocouples with in situ measurement of time constant and direct compensation by signal recording and analysis, using a micro-processor. Signal variation of velocity and temperature with time are directly recorded on the high-speed movie camera. Variation in location and amplitude of peaks of velocity and temperature traces are directly associated with flame structures recorded by film. Ionization probes are used for measurement of flame location and number density of ions. Signals from all probes are acquired and processed by PDP-8 and PDP-1103 Digital Equipment Corporation computers. Measurements have been made in the transitional region of the mixing zone of the round propane/air jet flame.

The size and velocity of droplets have been measured simultaneously by a particle counting Laser Doppler Anemometer (LDA) in kerosene fuel sprays under both burning and nonburning conditions. This measurement technique enables rapid measurement of size and velocity of particles in spray flames for particle diameters larger than the fringe spacing up to, at least, 300  $\mu\text{m}$ . The time dependent variations in local spray structure can be measured at particle counting rates of 2 kHz with spray densities of, at least,  $10^{10}$  particles/ $\text{m}^3$ . Particle sizes are derived from pulse height analysis of the mean LDA signals and velocities are determined simultaneously, by measuring Doppler shift frequencies. The performance and accuracy of the system is determined by analysis, using geometrical optics theory, coupled with calibrations using a monosized particle generator. The measurements demonstrate that droplet velocity is a function of droplet diameter for both burning and nonburning conditions. The technique enables temporally averaged local size distributions to be measured. Spatially averaged size distributions are derived from the simultaneously acquired velocity data. Comparison of results obtained under burning and nonburning conditions show changes in size distribution due to preferential vaporization of small droplets, acceleration due to thermal expansion of gases and corresponding changes in droplet momentum.

OVERVIEW OF THIRD INTERNATIONAL WORKSHOP  
ON LASER VELOCIMETRY (LV-III)  
AND  
LDV MEASUREMENTS AND ANALYSIS IN  
TURBULENT AND MIXING FLOWS  
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H.D. Thompson and W.H. Stevenson

School of Mechanical Engineering  
Purdue University  
West Lafayette, IN 47907

1. LV-III Summary

LV-III was held at Purdue University on July 11-13, 1978. The workshop was jointly sponsored by AFOSR, AMRDL, DOE and ONR. The program included twelve sessions with 52 prepared presentations and several informal comments on current work in progress. The theme of the workshop was the use of laser velocimetry in hostile environments. Technical sessions included:

- Developments in Instrumentation
- Data Analysis (2 sessions)
- Combustion Measurements
- Measurements in Turbulent Flows
- General Applications (2 sessions)
- Particle Diagnostics (2 sessions)
- Wild Card
- Summary Panel Discussion

Major conclusions of the workshop were:

1. The laser velocimeter is finding wide acceptance as a measuring instrument in difficult environments.
2. In difficult measuring situations the laser velocimeter needs to be carefully designed for the specific application.
3. Additional work remains to be done on data collection and analysis in highly turbulent and reacting flows. Significant questions of data biasing in turbulent flows remain.
4. The problem of in situ particle sizing using the fringe (laser velocimeter) method and other optical techniques is being studied by a number of groups. A great deal of progress has been made, but many questions remain.
5. The two-spot or dual-focus velocimeter is receiving more attention and is advantageous in some applications. Questions remain about its performance in highly turbulent flows.

Proceedings of the workshop will be published by the Hemisphere Publishing Corporation in a hardback volume and should be available about January 1979. Copies may be ordered from Hemisphere Publishing Corporation, 1025 Vermont Ave., N.W., Washington, D.C. 20005.

2. LDV Measurements and Analysis in Turbulent and Mixing Flows

The objective of this effort is to experimentally and analytically investigate the biasing of individual realization LDV (Laser Doppler Velocimeter) signals and to investigate the feasibility of the use of fluorescent dye tracers in the study of mixing and turbulence. The contract was initiated in April 1977. The LDV optical system design is for two velocity components using a two color, dual scatter, forward scatter design. Initial hardware has been constructed for only one component. A 5 watt argon laser is used. The LDV optical system provides for:

- X-Y-Z traverse using a motor driven mill table with digital position readout
- Bragg cell frequency shift in one or both beams
- Accurate positioning of focused beam waists at the beam intersection
- Control of probe volume size and beam intersection angle independent of focusing lens
- Polarization rotation to optimize beam polarization at the probe volume.

The data processor is either a high speed unit designed and built at Purdue or a TSI model 1980. For data recording, a dedicated micro computer facility built around an IMSAJ 80-80 micro computer is being used with a direct link to Purdue's main CDC-6500 facility for data processing.

The initial studies will be carried out in a flow channel over a rearward facing step (dump combustor). The test facilities are in the final stages of check-out.

Initial experimental studies will concentrate on indentifying and measuring biases arising in individual realization LDV measurements in highly turbulent flows by

- a) comparing results with and without frequency shifting;
- b) comparing measurements at different angles to the main stream flow,
- c) controlling the seeding particle size, distribution and concentration, and
- d) using fluorescent dye tracers in the seeding material.

A parallel analytical program is being conducted which consists of developing a turbulence model on the computer to study and compare the effects of the experimentally derived results.